

Kinetic Model of Cure Reaction and Filler Effect

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Synopsis

A new kinetic model for cure reactions has been developed from the concept of nonequilibrium thermodynamic fluctuation theory in which a distribution function relaxation spectrum is used for explaining cure kinetics of polymer–filler systems. It is found that an increase in filler loading reduces the relaxation time but broadens the relaxation spectrum of the cure reaction. The model is used to explain the cure curves which are obtained both from the Monsanto Rheometer 100 and the Rheometric Mechanical Spectrometer. Not only can the model predict scorch time, cure time, and activation energy of the cure reaction, but it can also take into account polymer–filler interaction and predict physical and mechanical properties of polymer systems during cure.

INTRODUCTION

Understanding and predicting cure kinetics of elastomeric or thermosetting materials is of practical interest both in the materials manufacturing process and the end-product performance. Unfortunately, in most polymeric systems, the cure reactions are quite complex; therefore, it is difficult for one to develop a kinetic model which can explain and predict changes of physical and mechanical properties of the polymer during the cure reaction. Although there have been many studies on cure kinetics, most of them are limited to the method of calorimetry,^{1–5} such as differential scanning calorimetry (DSC) or differential thermal analysis (DTA). Here, the definition of the state of cure is not directly correlated to the physical, mechanical, or rheological properties of polymers. Therefore, kinetic models, which are developed from the calorimetric method, are unable to predict properties, such as viscosity and dynamic modulus, which are used to determine the manufacturing operation and end-product performance of polymeric systems.

Conventionally, rules of thumb have been widely used in the industry for curing rubbers. It has been assumed that the rate of cure is doubled for every 10°C increase in cure temperature. In addition, cure time is increased 5 min for every 0.25 in. of thickness to the center of a molding.^{6,7} In general, these rules do not apply to most polymeric systems because the phenomena of heat transfer and cure kinetics have been oversimplified. The cure rate depends on the basic polymers, curatives, cure temperature, and filler loading. The prediction of cure rate will be discussed from a new model of cure kinetics which is developed from the concept of a nonequilibrium thermodynamic fluctuation theory of chemical relaxation.

KINETIC THEORY OF CURE

Crosslinking of Natural Rubber

The chemistry of natural rubber vulcanization is so complex that it is difficult to have a comprehensive understanding of the cure reaction. Nevertheless, in the last two decades, rubber scientists have unravelled some of the major reactions during cure. For example, accelerated sulfur vulcanization has been thought to proceed by the following steps⁸⁻¹²:

1. The accelerator reacts with sulfur to give monomeric polysulfides of type $\text{Ac-S}_x\text{-Ac}$, where Ac is an organic radical derived from the accelerator.

2. The polysulfides can interact with rubber to give polymeric polysulfides of the type $\text{Rubber-S}_x\text{-Ac}$.

3. The rubber polysulfides then react, either directly or through a reactive intermediate, to give crosslinks or rubber polysulfides of the type $\text{Rubber-S}_x\text{-Rubber}$.

As has been known, elastomer vulcanization by sulfur with no accelerator is no longer of commercial significance because of the long cure time. Different types of accelerators give different scorch rates (premature cure) and cure rates during crosslinking. The crosslink types and chain modifications of sulfur vulcanization in natural rubber may be present as monosulfide, disulfide, polysulfide, pendant sulfides, cyclic monosulfides, and cyclic disulfides.⁹

The formation of a crosslinking structure leads to the conclusion that if desulfuration proceeds rapidly, the final network will be highly crosslinked with mainly monosulfidic bonds. Such a network is termed efficiently crosslinked. On the other hand, if desulfuration proceeds slowly, there will be opportunities for thermal decomposition. These networks are inefficiently crosslinked. For the vulcanization of natural rubber, if the temperature rises above 160°C, reversion or inefficiently crosslinked networks might be present.

Kinetic Model of Cure Reaction

Recently DSC has been used in the study of the cure kinetics in thermosets.¹⁻⁵ In the study of cure kinetics by the method of calorimetry, a quasitheoretical model is proposed to describe the dependence of the cure rate on the curing temperature and time by analyzing the amount of heat evolved isothermally as a result of the cure reaction. The kinetic model of cure is expressed as⁵

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (1)$$

where K_1 and K_2 are rate constants and m and n are constants independent of temperature. The relative degree of cure α is defined by

$$\alpha = Q_R/Q_m \quad (2)$$

where Q_R is the amount of heat evolved isothermally as a result of the reaction from time $t = 0$ to t and Q_m is the total amount of heat generated or the isothermal heat of cure. It may be temperature-dependent. Kamal et al.⁵ were able to use the above model for satisfactorily describing the data from DSC experiments for both epoxy and unsaturated polyester systems. However, the definition of the degree of cure, which is given in eq. (2), does not have a direct

correlation with the physical or mechanical properties of polymers during a complete isothermal cure cycle. Moreover, the cure kinetics of polymeric materials not only depend on cure systems but also on filler loading. Since the physical and mechanical properties of elastomeric thermosets depend on the thermal history of cure, it is of practical interest to develop a kinetic model which can predict the physical and mechanical properties during cure.

Although both Craig¹³ and Mussatti and Macosko¹⁴ have developed a kinetic model for predicting viscosity and modulus during the cure reaction, the application of this model is limited because this model does not include polymer-filler interaction. This model is also limited to first order or single relaxation function type of chemical reactions. Therefore, in the following, we will develop a general relaxation function for explaining cure kinetics with polymer-filler interaction included in the model.

As has been discussed by Hsich,¹⁵ any chemical relaxation (reaction) can be explained from irreversible thermodynamic fluctuation theory, in which changes of physical and mechanical properties during the chemical reaction can be interpreted and predicted from the mean square fluctuations of thermodynamic ordering parameters. Here the thermodynamic ordering parameter ξ is thermodynamically conjugated to thermodynamic affinity A .^{16,17} During chemical relaxation, one can observe and measure changes of physical and mechanical properties of the chemical system from the time correlation function of the mean square fluctuations of ordering parameters. For example, a change of chemical-reaction ordering parameters will result in a change of volume or compressibility. This in turn will result in excess ultrasonic absorption and dispersion. This can be observed experimentally by ultrasonic methods. In addition, one also observes a variation in dielectric constant with a change in chemical-reaction ordering parameters. This will lead to excessive light scattering and can be measured experimentally by laser techniques.¹⁵ Accordingly, one can develop a kinetic model of cure reaction for elastomeric or thermosetting materials based on the concept of nonequilibrium thermodynamic fluctuation theory.

The cure reaction can be considered as multiple chemical reactions in which each chemical reaction is associated with a thermodynamic ordering parameter ξ_i . Then variations of physical or mechanical properties during cure can be expressed as the time correlation function of the mean square fluctuations of ordering parameters. There is a similarity between the kinetic process of cure and the molecular structural relaxation process, which was discussed by Hsich, Montrose, and Macedo¹⁸ and Hsich,¹⁹ based on the same concept of nonequilibrium thermodynamics. Thus, the physical or mechanical properties of polymer systems during cure can be expressed as

$$\frac{P_\infty - P(t)}{P_\infty - P_0} = \sum_i W_i \langle (\Delta_i \xi)^2 \rangle \exp \left[- \left(\frac{t}{\tau_i} \right) \right] \quad (3)$$

Let

$$g_i = W_i \langle (\Delta_i \xi)^2 \rangle \quad (4)$$

Then

$$\frac{P_\infty - P(t)}{P_\infty - P_0} = \sum_i g_i \exp[-(t/\tau_i)] \quad (5)$$

where P_0 and P_∞ are the initial and final physical or mechanical properties during cure, $P(t)$ is the property at time t , $\langle \Delta \xi_i \rangle^2$ is the mean square fluctuation of the ordering parameter ξ_i , W_i , and g_i are the weight constants, and τ_i is the relaxation time of the chemical reaction associated with ordering parameter ξ_i .

As has been discussed,^{18,19} implicit in eq. (5) is the normalization $\sum_i g_i = 1$. It is useful to generalize this from a sum of single relaxation processes to a continuous distribution of such processes; then the distribution function relaxation spectrum for the analog of eq. (5) is

$$[P_\infty - P(t)] / (P_\infty - P_0) = \exp[-(t/\tau)^\beta] \quad (6)$$

where β is the constant describing the width of the relaxation spectrum.

EXPERIMENTAL RESULTS AND DISCUSSION

The following recipe for a natural rubber compound is used for the study of cure kinetics:

<i>Ingredient</i>	<i>phr</i>
SMR 5CV	100
Reogen	1
Stearic acid	1
Zinc oxide	5
Agerite HP—S	1
Agerite resin D	1
Flexzone 3C	1.5
Wax	2
NOBS special	0.9
Monex	0.2
Sulfur	1.1
Dicup 40C	2

The filler loading in this study is varied from 0 to 60 phr of N330 carbon black. Cure curves which were taken from the Monsanto Rheometer 100 for three different temperatures, 130°C, 150°C, and 170°C, are shown in Figures 1–7 for seven different filler loadings. As one can see from the figures, the cure curves for these three different temperatures present three different types of cure behavior: marching cure curve (at 130°C), normal cure curve (at 150°C), and reversion cure curve (at 170°C). This unusual cure behavior is due to a complex cure reaction in natural rubber, as was mentioned earlier. Therefore, some difficulty might be expected in developing a kinetic model for predicting all three different types of cure curves.

In reality, more than one distribution function should be used in the model to consider both the marching and reversion behavior of the cure reaction. However, in practice, it would be less desirable to include too many parameters in the model because it will reduce the convenience and effectiveness in applying the model to practical applications. Therefore, only one distribution function, as shown in eq. (6), will be used in the model to explain and predict cure kinetics. Each of the two parameters (β and τ) will have its own physical significance or meaning in explaining the kinetic process of cure in polymer–filler systems.

The cure curves which are obtained from the Monsanto Rheometer 100 are

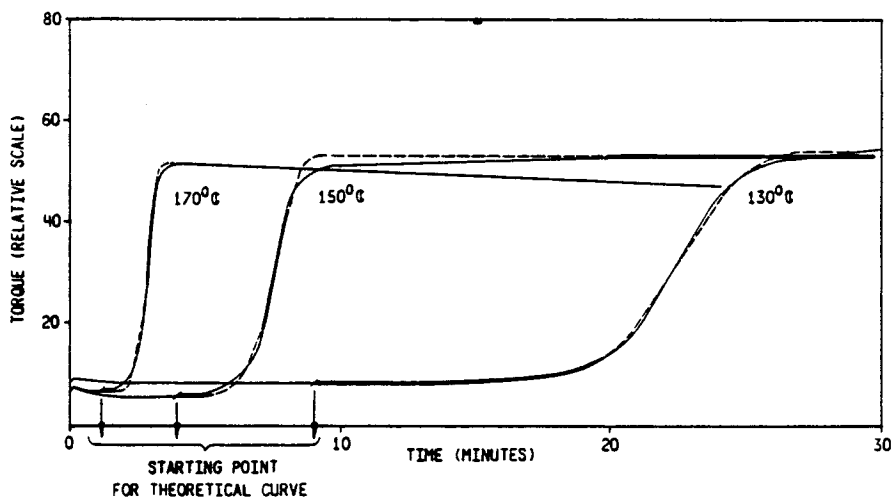


Fig. 1. The Monsanto cure curve for 0 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

expressed as torque (required to oscillate the sample) vs. curing time. Here the torque is equivalent to the modulus of the sample during cure. Hence the following equation rewritten from eq. (6) is

$$[G_{\infty} - G(t)] / (G_{\infty} - G_0) = \exp[-(t/\tau)^{\beta}] \quad (7)$$

and

$$\tau = \tau_0 \exp(H/RT) \quad (8)$$

where τ_0 is constant, R is the gas constant, T is the absolute cure temperature, and H is the activation energy of the cure reaction. G is the shear modulus or any modulus which is equivalent to the torque in the Monsanto cure curve.

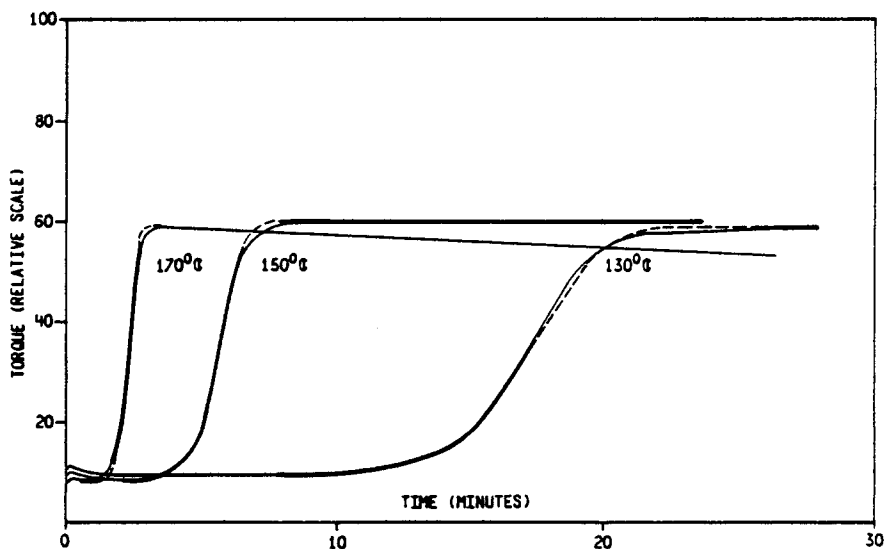


Fig. 2. The Monsanto cure curve for 10 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

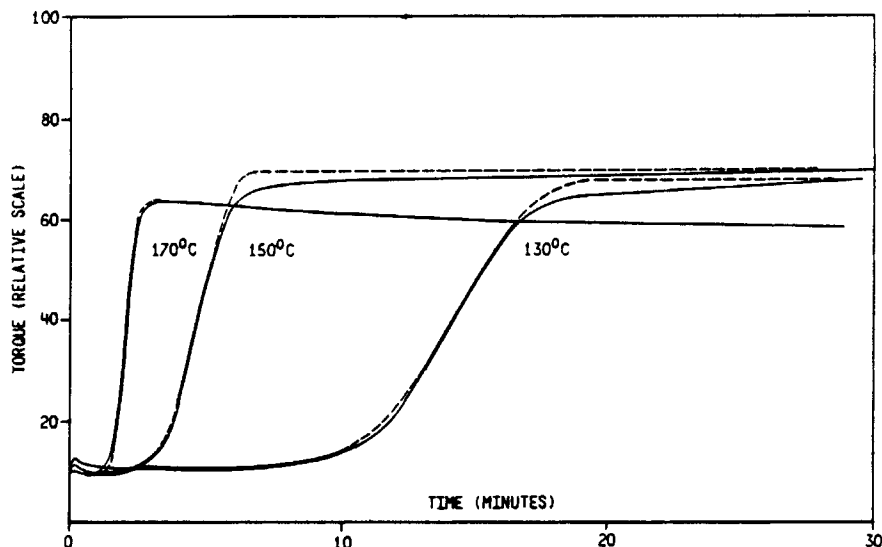


Fig. 3. The Monsanto cure curve for 20 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

It should be noted that the torque in the cure curve decreases to a minimum value at the beginning before it starts to increase. This is due to the fact that the modulus or viscosity of the sample at room temperature is higher than at the cure temperature before crosslinking begins. Therefore, in fitting cure curves, the induction time t_0 (which is the time for the torque to reach a minimum value) must be subtracted from t in eq. (7). Then eq. (7) is modified as

$$\frac{G_\infty - G(t)}{G_\infty - G_0} = \exp \left[- \left(\frac{t - t_0}{\tau} \right)^\beta \right] \quad (7a)$$

or

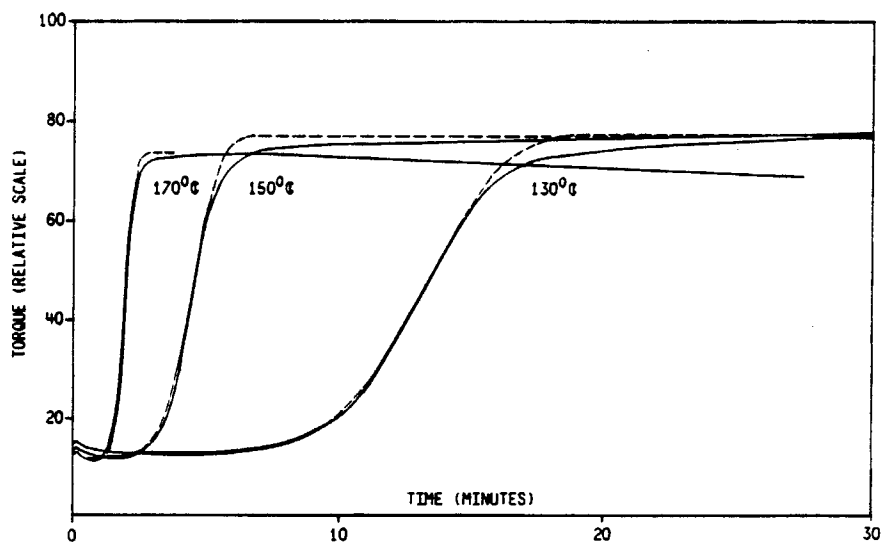


Fig. 4. The Monsanto cure curve for 30 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

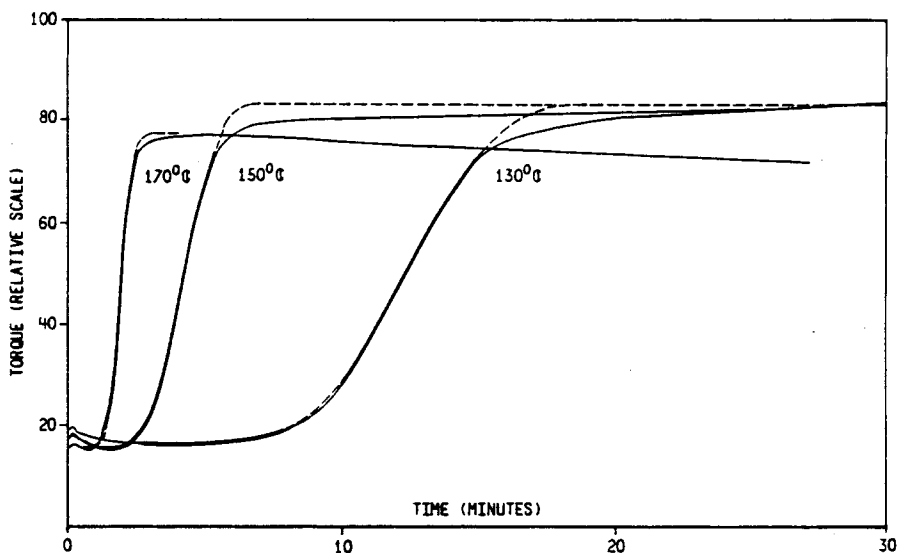


Fig. 5. The Monsanto cure curve for 40 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

$$G(t) = G_0 + (G_\infty - G_0) \left\{ 1 - \exp \left(\frac{t - t_0}{\tau} \right)^\beta \right\} \quad (7b)$$

By using eq. (7b), τ can be obtained from the cure curve by calculating the value of $G(t)$ at $t = t_0 + \tau$. The calculation for $G(t_0 + \tau)$ is

$$G(t_0 + \tau) = G_0 + (G_\infty - G_0)(1 - e^{-1}) \quad (9)$$

where G_0 and G_∞ are the minimum and maximum values of torque on the cure curve. The values of τ for rubber compounds at various filler loadings and cure temperatures are listed in Table I. The relationship between relaxation time

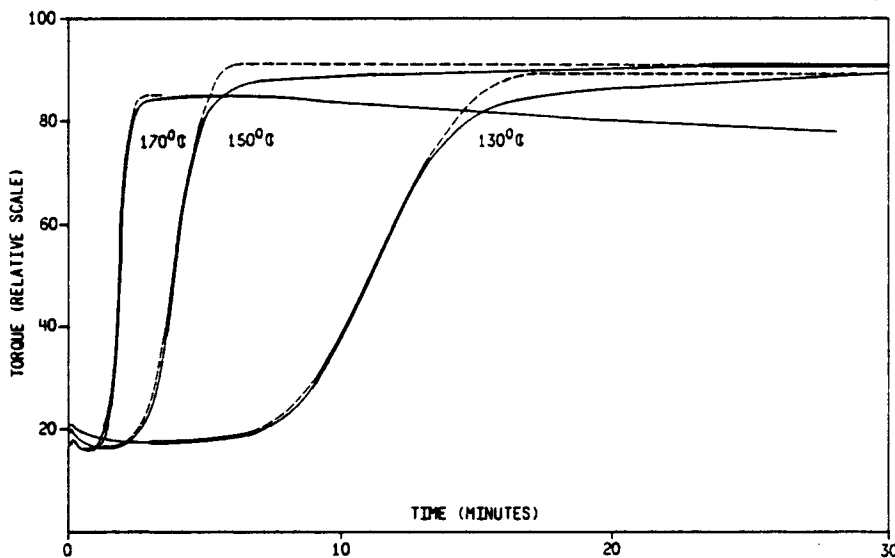


Fig. 6. The Monsanto cure curve for 50 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

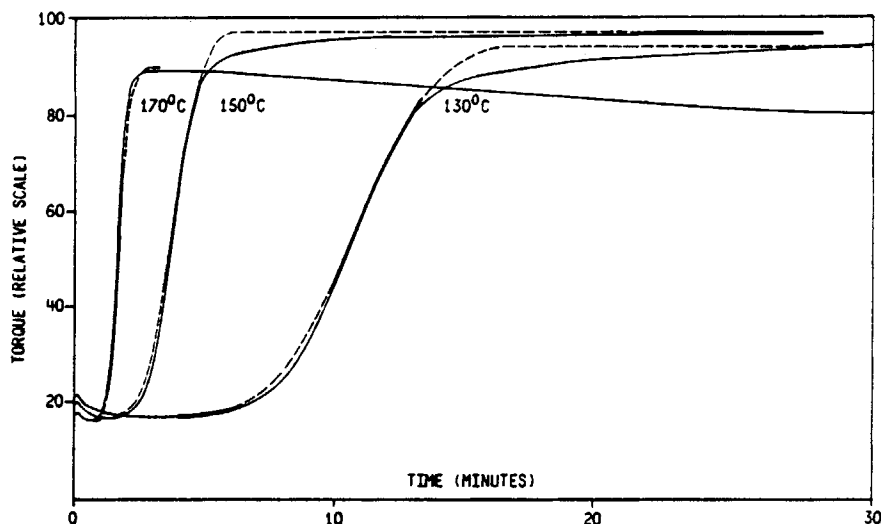


Fig. 7. The Monsanto cure curve for 60 phr of carbon black loading: (—) experimental data; (---) theoretical calculation.

τ and the cure temperature T is satisfactory for an Arrhenius equation, as shown in eq. (8). The activation energy remains a constant value of $H = 18$ kcal/mol (75.3×10^3 J/mol) with various filler loadings. But τ_0 decreases as filler loading increases. This finding demonstrates that the increase of filler loading serves to accelerate the cure reaction, and, therefore, the cure time is reduced. The values of τ_0 for various filler loadings are plotted in Figure 8 and also listed in Table I.

After τ has been determined, eq. (7b) is reduced to only a single parameter (β) equation. A method of least squares is used to fit eq. (7b) to all cure curves. The best fits from the theoretical calculation of eq. (7b) are also plotted in Figures 1-7. The theoretical prediction shows good agreement with experimental results. (For the cure curves with reversion behavior, the theoretical calculation is only up to the curing time of the maximum torque.) The values of β for various filler loading determined from the best fit are plotted in Figure 9 and also listed in Table I. The result shows that the increase of filler loading reduces the value of β and, therefore, broadens the relaxation spectrum. This leads to the same conclusion as the results from previous studies on the viscosity of elastomer-filler interaction.²⁰ Since the value of β is larger than 1, we can also conclude that the cure reaction is not a first-order but a high-order chemical reaction. Therefore, the result of this study leads us to conclude that the loading of filler tends to broaden the relaxation spectrum but reduces the relaxation time (with the same activation energy) for the curing reaction.

We have demonstrated that the new model can explain reasonably well the process of crosslinking. It can predict cure time for a particular degree of cure which can be defined by the physical or mechanical properties during cure as has been shown in eq. (7a) or (7b). Nevertheless, we would like to extend the model to predict the scorch time (premature cure), which is of vital importance in polymer processes such as mixing, transfer molding, and injection molding. Here the scorch time is defined as the time for the torque of the cure curve to reach 5% of the total relaxation strength, i.e., $0.05 (G_\infty - G_0)$, above the minimum

TABLE I

Filler loading (phr)	Temp (°C)	t_0 (min)	τ (min)	τ_0 ($\times 10^{-9}$ min)	H (kcal/mol)	β	t_s (min)	τ_{s0} ($\times 10^{-9}$ min)	τ_s (min)
0	130	8.10	15.10	3.02	18	7.72	18.25	3.65	18.25
	150	2.51	5.25				6.09		6.34
	170	1.03	2.01				2.40		2.43
10	130	5.12	12.84	2.57	18	5.92	12.79	2.56	12.79
	150	1.42	4.47				4.13		4.45
20	170	0.71	1.71				1.75		1.70
	130	3.60	11.42	2.28	18	4.74	9.70	1.94	9.70
30	150	1.07	3.97				3.19		3.37
	170	0.77	1.52				1.58		1.29
	130	3.62	10.42	2.08	18	4.29	8.83	1.76	8.83
40	150	1.15	3.63				2.96		3.08
	170	0.73	1.39				1.43		1.18
	130	3.46	9.77	1.95	18	3.94	8.05	1.61	8.05
50	150	1.16	3.40				2.76		2.80
	170	0.78	1.30				1.39		1.07
	130	3.43	8.80	1.76	18	3.67	7.34	1.47	7.34
60	150	1.22	3.06				2.58		2.55
	170	0.78	1.17				1.30		0.98
	130	3.50	8.00	1.60	18	3.29	7.15	1.43	7.15
170	150	1.25	2.78				2.53		2.48
	170	0.70	1.06				1.18		0.95

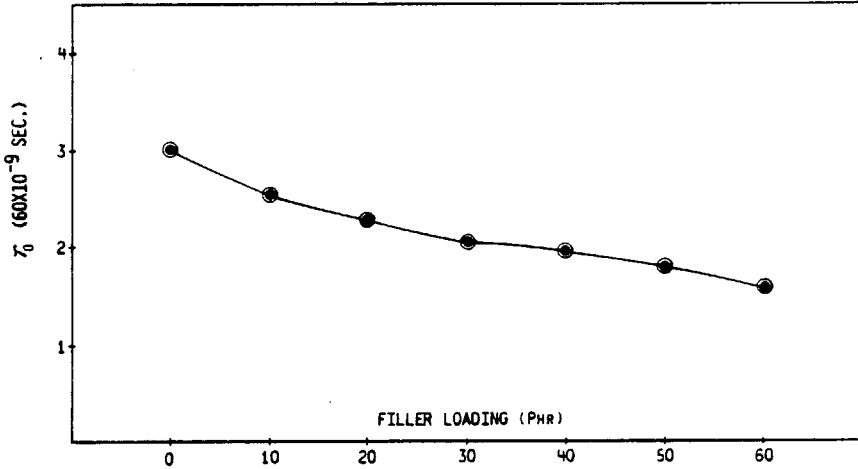


Fig. 8. τ_0 vs. various carbon black loading.

value of torque G_0 .⁶ Therefore, the experimental scorch time t_5 can be obtained from the cure curve when the value of $G(t)$ is

$$G(t_5) = G_0 + 0.05(G_\infty - G_0). \quad (10)$$

The scorch times t_5 for all cure curves in Figures 1-7 for various temperatures and filler loadings are listed in Table I. The theoretical calculation of the scorch time τ_s , from an Arrhenius equation, is given as

$$\tau_s = \tau_{s0} \exp(H/RT) \quad (11)$$

where τ_{s0} is the constant. In calculating scorch time τ_s , the same activation energy for the cure reaction, $H = 18$ kcal/mol, is also used for the scorch reaction; and the scorch time t_5 at a temperature of 130°C from the experimental data of

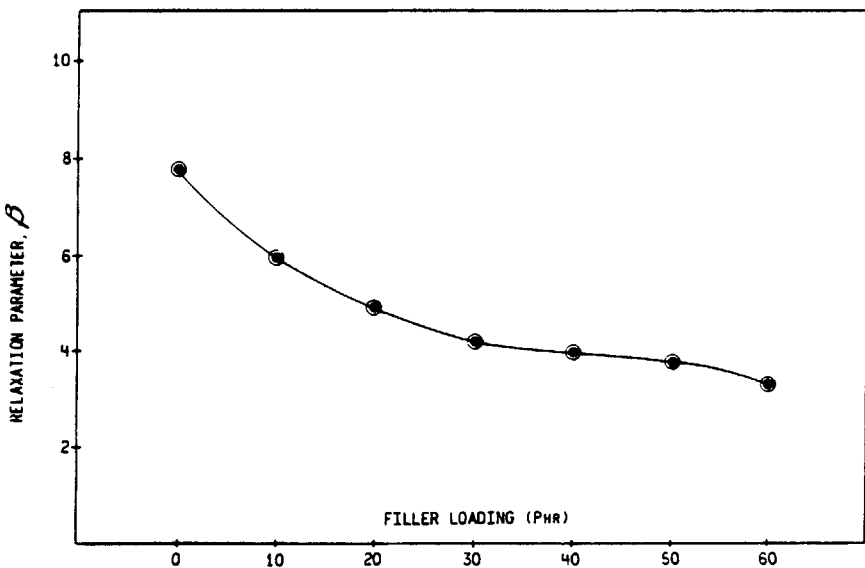


Fig. 9. β vs. various carbon black loading.

cure curve is used as a reference for determining the constant of τ_{s0} for various filler loadings. After the value of τ_{s0} for various filler loadings is determined, the theoretical prediction of the scorch time τ_s at various temperatures and filler loadings can be calculated from eq. (11). The result of the calculation for the values of τ_{s0} and τ_s are listed in Table I. It can be seen from the comparison of the values for t_5 and τ_s in Table I that the theoretical predictions of the scorch times are in good agreement with the experimental results. The value of τ_{s0} for various filler loadings is also plotted in Figure 10. The behavior of τ_{s0} is like τ_0 , which decreases as filler loading increases; therefore, filler loading also reduces the scorch time as it does the cure time. It should be noted here that the difference between the experimental and theoretical result of the scorch time is higher at 170°C (less than 0.33 min). This might be due to a reversion of the cure curve at this temperature.

So far, we have developed a model of cure kinetics for explaining the cure curve obtained from a Monsanto Rheometer 100. The model allows us to predict scorch time, cure time, and activation energy of cure at various filler loadings. Since end-product performance is governed by dynamic mechanical properties of polymer systems during cure, it is desirable to extend the new model to predict actual dynamic mechanical properties at various cure times. In order to do this, the data of the storage part of the dynamic shear modulus G' during cure were obtained from the Rheometric Mechanical Spectrometer (RMS). The experimental data for two different filler loadings at temperatures of 130°C and 150°C are shown in Figures 11 and 12.

For fitting the data from RMS, the storage dynamic shear modulus G' was substituted for G in eq. (7b). Then the same activation energy H and parameter β from Table I were used in the modified equation (7b) for predicting G' as a function of cure temperature and time for two different filler loadings. $\beta = 4.29$ and 3.94 were used for the rubber compounds with filler loadings of 30 phr and 40 phr, respectively. Results of the theoretical calculation are plotted in Figures 11 and 12 along with the experimental data. There is good agreement between the theoretical projections and the experimental data. It should be noted that τ_0 values here are different from the values of previous calculations for the data

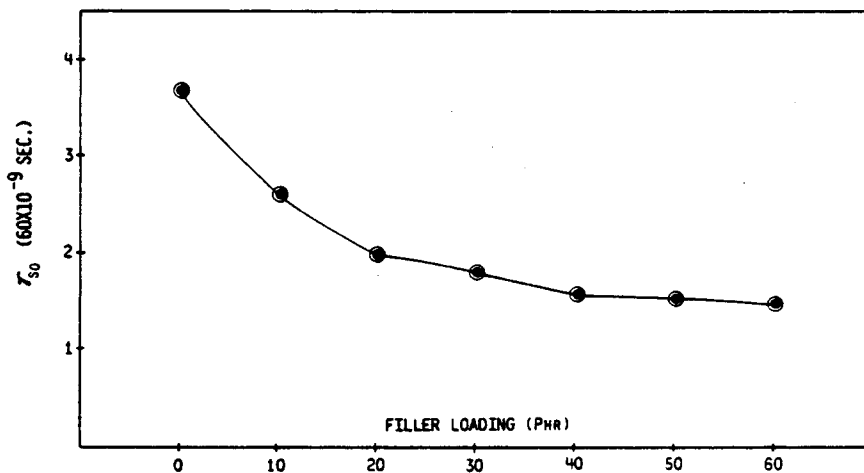


Fig. 10. τ_{s0} vs. various carbon black loading.

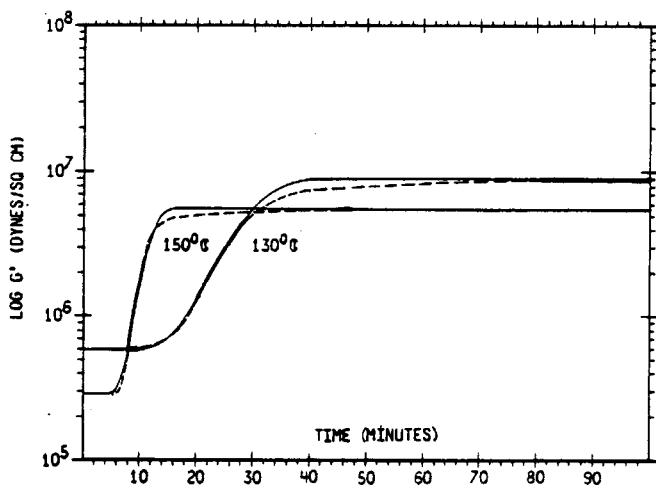


Fig. 11. The storage shear modulus G' vs. curing time for 30 phr of carbon black loading: (—) experimental data; (----) theoretical calculation.

obtained from the Monsanto Rheometer 100. The values of τ_0 are 4.99×10^{-9} min and 4.59×10^{-9} min for rubber with filler loadings of 30 phr and 40 phr, respectively. These differences might be due to variations in experimental measuring conditions, keeping in mind that the dynamic mechanical properties predicted in this study are at cure temperature. The dynamic mechanical properties of elastomers at various temperatures and filler loadings under the same conditions of cure will be discussed elsewhere.

CONCLUSION

A model of cure kinetics has been developed from the concept of a nonequilibrium thermodynamic fluctuation theory of chemical relaxation. In this model a distribution function relaxation spectrum is used to explain the kinetic process

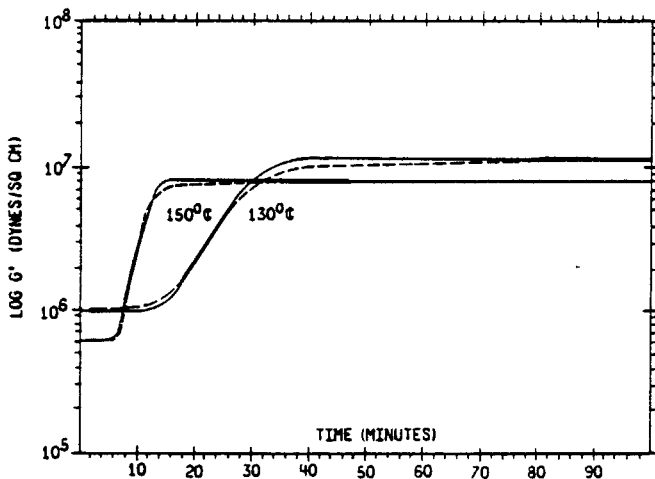


Fig. 12. The storage shear modulus G' vs. curing time for 40 phr of carbon black loading: (—) experimental data; (----) theoretical calculation.

during the cure reaction. The model allows us to predict the scorch time, cure time, and activation energy of the cure reaction for various filler loadings. The model also is used to predict dynamic mechanical properties during cure. This opens up the possibility of achieved end-product performance by programming the desired dynamic mechanical properties according to the kinetics of cure at various cure temperatures and times. The conclusions from this study on cure kinetics are:

1. The filler loading has an insignificant effect on the activation energy of the cure reaction.
2. The same activation energy for the cure reaction can be used to predict scorch time.
3. An increase in filler loading reduces the relaxation time but broadens the relaxation spectrum of the curing reaction.
4. An increase in filler loading also reduces scorch time.

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