

## The Chemistry of Sulfur Curing. Part I. Kinetics of Vulcanization of an EPDM Elastomer Accelerated by Zinc Dimethyldithiocarbamate\*

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### Synopsis

The maximum cure rates of an EPDM rubber were determined by using the Monsanto oscillating disk rheometer and correlated against the initial concentrations of curing ingredients. Unaccelerated and ZnDMDC-accelerated sulfur curing systems were used. The results were interpreted to indicate that both unaccelerated and ZnDMDC-accelerated curing reactions proceed simultaneously in ZnDMDC-accelerated stocks. The maximum cure rates of the ZnDMDC-accelerated crosslinking reactions were found to be first-order in initial ZnDMDC concentration, second-order in initial cure site concentration, variable fractional order in initial sulfur concentration, and approximately zero-order in initial zinc oxide concentration. The maximum cure rates of the ZnDMDC-accelerated reaction were shown to be limited by the low solubility of ZnDMDC in the polymer. The maximum cure rates of the unaccelerated crosslinking reaction were found to be 0.6-order in initial sulfur concentration, 1.2-order in initial cure site concentration, and of a positive variable order in initial zinc oxide concentration.

### INTRODUCTION

The kinetics of vulcanization of an ethylene-propylene-diene terpolymer (EPDM) elastomer were measured with the aid of the Monsanto oscillating disk rheometer.<sup>1</sup> The EPDM elastomer used in the study was Nordel† 1070 hydrocarbon rubber<sup>2-4</sup> (manufactured by E. I. du Pont de Nemours & Company, Inc.).

The Monsanto oscillating disk rheometer is one of a number of instruments developed in the past several years which enable the measurement of elastomer stiffness during the vulcanization process. These instruments lend themselves readily to the measurement of the kinetics of the vulcanization process by providing information on the change of polymer stiffness as a function of cure time. The use of such instruments for the study of vulcanization kinetics has been demonstrated by Scheele and Hillmer<sup>5</sup> using the Agfa Vulkameter and by Coran<sup>6</sup> using both the Agfa Vulkameter and the Monsanto oscillating disk rheometer.

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† DuPont's registered trademark for its hydrocarbon rubber.

The EPDM polymer used in this study, Nordel 1070 hydrocarbon rubber, is an ethylene-propylene-1,4-hexadiene terpolymer. Nordel 1070 has a Mooney viscosity at 121.1°C. (250°F.) of 70. The polymer was extensively extracted with acetone prior to being used in the kinetic experiments in order to remove any materials which could alter its curing behavior. The vulcanization studies were carried out on gum polymer containing varying amounts of zinc oxide, sulfur, and zinc dimethyldithiocarbamate accelerator.

The kinetic data obtained in this investigation were correlated with the curing system variables in the following manner. The maximum rates of cure of EPDM polymer compounds were determined from the rheometer data. By varying the initial concentrations of the components of the curing systems, the maximum rates of cure could be varied. Relationships could thus be obtained between the maximum rates of cure and the initial concentrations of any of the components of the curing systems. This technique is a variation of the well-known method of kinetic analysis in which the initial rates of reaction are correlated with the initial concentrations of the reaction components. Due to the induction periods present in most vulcanization reactions, it is not possible to use the initial cure rates; the next best approximation, the maximum cure rates, must be employed.

The maximum cure rates,  $(\Delta M/\Delta t)_{\max}$ , of the EPDM polymer compounds were determined by measuring the maximum slopes of the modulus versus time curves of the oscillating disk rheometer plots. A typical oscillating disk rheometer plot is shown in Figure 1. The maximum slope is found by moving a straight edge tangent to the rheometer curve and drawing in the tangent where it is at a maximum.

In their work on the curing of natural rubber, Scheele and Hillmer<sup>5</sup> and Coran,<sup>6</sup> after allowing for induction periods, were able to obtain linear

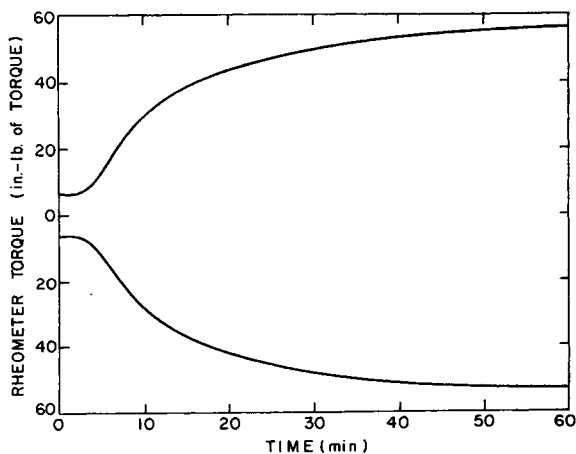


Fig. 1. Monsanto oscillating disk rheometer plot of an EPDM gum stock cured at 160°C.

first-order plots of the rates of curing as measured by changes in rheometer torque. First-order plots of log rheometer torque versus time for our systems were not simple straight lines, so that it was not possible to assign a simple first-order rate constant to the crosslinking reaction. Thus the use of the maximum cure rate technique was preferred for the analysis of the EPDM polymer kinetic data.

## EXPERIMENTAL

### Materials Used

**EPDM Polymer.** Nordel 1070 hydrocarbon rubber is sold by E. I. du Pont de Nemours and Company.

**EPM Copolymer.** EPR-404 is sold by Enjay Chemical Company.

**Zinc Dimethyldithiocarbamate (ZnDMDC).** Methyl Zimate (ZnDMDC) is sold by R. T. Vanderbilt Company, Inc.

**Sulfur.** Tube\* brand refined (soft) rubber compound sulfur is sold by the Stauffer Chemical Company.

**Zinc Oxide.** Horse Head Kadox† 15 zinc oxide is sold by the New Jersey Zinc Company.

### Polymer Extraction

The Nordel 1070 was cut into  $\frac{1}{4} \times \frac{1}{4}$  in. or smaller pieces and extracted for 7 days with acetone by use of Soxhlet extractors. The polymer was freed of acetone in a vacuum over at 60°C. for 24 hr.

### Compounding

The curing ingredients were mixed into the polymers by using a 4 × 8 in. rubber mill. Considerable care was needed to ensure uniform dispersion of the solid materials in the polymers. Non-uniform dispersion is a major source of error in this type of kinetic study. The EPDM-EPM blends were prepared by using a 4 × 8 in. rubber mill. The polymer blends were extensively milled at 25°C. and at 100°C. before curing agents were added.

### Monsanto Oscillating Disk Rheometer

The Monsanto rheometer has been described elsewhere.<sup>1</sup> A model LS rheometer was used in this study.

### Kinetic Runs

Rheometer samples 2 in. square were died out from  $\frac{1}{4}$ -in. thick compounded stocks. The Monsanto rheometer mold with the rotor inserted was closed and brought to the desired curing temperature. The mold was opened, the sample inserted, and the mold closed as rapidly as possible. After 60 sec. the mechanisms activating the oscillating rotor

\* Registered trademark of Stauffer Chemical Company.

† Registered trademark of New Jersey Zinc Company.

and the torque recorder were switched on. A recording was made of the torque on the rotor with time. A period of approximately 3–5 min. is required for the stock in the rheometer mold to come to a curing temperature of 160°C. All measurements were made at the low-frequency rotor speed (3 cpm).

A major source of operating error in using the rheometer arises from a slow chemical polishing of the biconical rotor. If suitable precautions are not taken, the chemical polishing of the rotor eventually results in slippage between the rotor and the polymer sample. Slippage problems were controlled by lightly sandblasting the rotor before each series of kinetic runs. Control stocks were run before and after each series of kinetic runs to check for slippage, excessive rotor wear due to sandblasting, and other nonrandom errors.

## EXPERIMENTAL RESULTS

### Cure Rate versus Zinc Dimethyldithiocarbamate Concentration

A typical logarithmic plot of the maximum cure rates of the EPDM polymer versus the initial concentrations of zinc dimethyldithiocarbamate (ZnDMDC) accelerator in the polymer is shown in Figure 2. The maximum cure rates increase with increasing initial ZnDMDC concentration up to certain limiting values and then cease to change with increasing ZnDMDC concentration. The limiting initial ZnDMDC concentrations above which the maximum cure rates cease to change are a function of the cure temperature, a higher cure temperature resulting in a higher limiting initial ZnDMDC concentration.

A likely cause of the maximum cure rate ceasing to increase above certain limiting ZnDMDC concentrations is that the solubility limit of ZnDMDC in the compounded polymer is being exceeded. To check this possibility the solubility limits of ZnDMDC in the EPDM polymer were

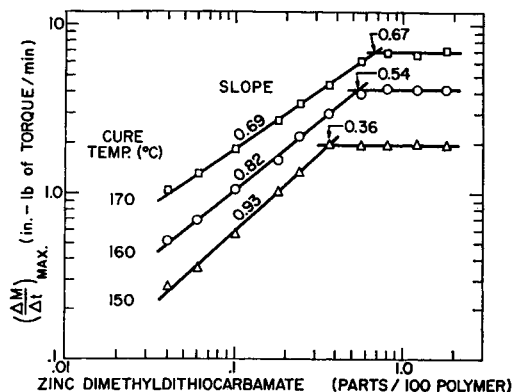


Fig. 2. Maximum cure rates vs. initial ZnDMDC concentrations. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5; ZnDMDC, as noted.

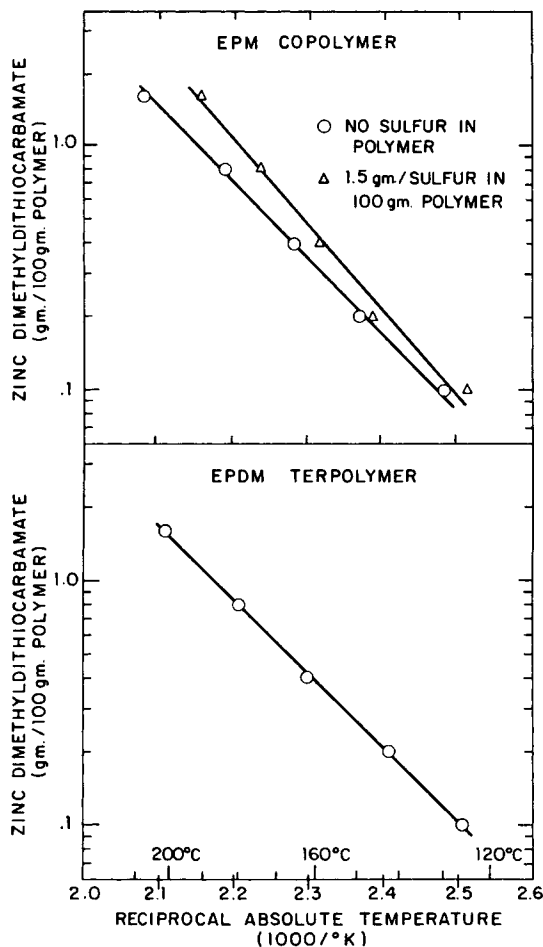


Fig. 3. Solubility of ZnDMDC in EPM copolymer and EPDM terpolymer as a function of temperature.

determined. The solubility measurements were made with the aid of a hot stage microscope by observing the temperature at which the ZnDMDC particules in a thin film of EPDM polymer disappeared. The temperatures of disappearance were determined at several ZnDMDC concentrations. Similar measurements were made with ethylene-propylene (EPM) copolymer elastomer, with and without added sulfur, in order to determine the effect of the added sulfur on the solubility of ZnDMDC. Solubility measurements were not made with EPDM polymer containing added sulfur due to possible complications caused by curing reactions. The results of the solubility measurements are shown in Figure 3. The heats of solution of ZnDMDC as calculated by using the van't Hoff equation were found to be 14 kcal./mole in both the EPDM polymer and the EPM copolymer in the absence of added sulfur. It should be noted that the

TABLE I  
Solubility Limits of ZnDMDC in EPM and EPDM Polymers

Polymer	Sulfur, g./100 g. polymer	Solubility limits of ZnDMDC, g./100 g. polymer		
		150°C.	160°C.	170°C.
EPDM		0.27	0.39	0.56
EPM		0.22	0.32	0.47
EPM	1.5	0.28	0.44	0.67
EPDM	1.5	0.34 <sup>a</sup>	0.54 <sup>a</sup>	0.80 <sup>a</sup>

<sup>a</sup> Estimated on the assumption that the addition of 1.5 g. of sulfur to 100 g. of EPDM polymer will produce the same percentage increase in the solubility of ZnDMDC in the EPDM polymer as it did in the solubility of ZnDMDC in the EPM copolymer at the same temperature. /

ZnDMDC solubility limits reported in this paper are not equilibrium solubility limits. The interpolated solubility limits of ZnDMDC at the curing temperatures used in this study are listed in Table I.

A comparison is shown in Table II of the kinetically measured limiting initial ZnDMDC concentrations above which the maximum cure rates cease to increase with increasing initial ZnDMDC concentrations and the solubility limits of ZnDMDC in the EPDM polymer as interpolated from the hot stage microscope measurements. The two sets of numbers agree quite closely. On the basis of the observed agreement, it is concluded that the maximum cure rates cease to increase above certain limiting initial ZnDMDC concentrations due to the solubility limits of ZnDMDC being exceeded.

TABLE II  
Solubility Limits of ZnDMDC in EPM Polymer,<sup>a</sup>  
Kinetic vs. Hot Stage Microscope Measurements

Method of measurement	Solubility limits of ZnDMDC, g./100 g. polymer		
	150°C.	160°C.	170°C.
Kinetic	0.36	0.54	0.67
Microscopic <sup>b</sup>	0.34	0.54	0.80

<sup>a</sup> Solubility limits of ZnDMDC in EPDM polymer which contains 1.5 g. sulfur/100 g. polymer.

<sup>b</sup> From Table I.

Below the solubility limits of ZnDMDC, the maximum cure rates are a function of the initial ZnDMDC concentrations. The slopes of the lines relating maximum cure rates to initial accelerator concentrations increase as the cure temperature is decreased, from a slope of 0.69 at 170°C. to a slope of 0.93 at 150°C. These line slopes are related to the kinetic order of the maximum cure rate with respect to the initial ZnDMDC concentration.

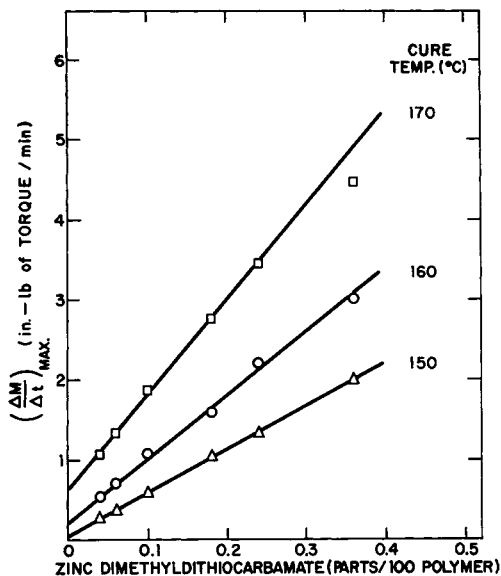


Fig. 4. Arithmetic plot of maximum cure rates vs. initial ZnDMDC concentrations. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5; ZnDMDC, as noted.

The data of Figure 2 at low initial concentrations of ZnDMDC, below the solubility limits, are replotted in Figure 4 on an arithmetic basis. The arithmetic plot allows extrapolation to zero accelerator concentration. The straight-line arithmetic relationships between maximum cure rates and initial accelerator concentrations in Figure 4 indicate that the maximum cure rates are first-order in initial ZnDMDC concentration. The greater than zero intercepts at zero accelerator concentrations for the 160 and 170°C. cures are indicative of the presence of a curing reaction at these temperatures which is independent of the ZnDMDC accelerator. Support for this interpretation of the data was obtained by measurement of the maximum cure rates of Nordel stocks containing only zinc oxide and sulfur with no ZnDMDC accelerator present. In Table III is shown a comparison

TABLE III  
Unaccelerated Maximum Cure Rates vs. the Zero  
Accelerator Intercepts of ZnDMDC-Accelerated Stocks

Cure temp., °C.	Unaccelerated maximum cure rates, in.-lb. of torque/min. <sup>a</sup>	Extrapolated to zero accelerator, maximum cure rates from Fig. 4, in.-lb. of torque/min.
170	0.64	0.62
160	0.29	0.21
150	0.10	0.05

<sup>a</sup> EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5.

of the values of the extrapolated intercepts of the ZnDMDC-accelerated cures and the measured maximum cure rates of the unaccelerated sulfur cures. The two sets of numbers agree quite well.

Knowing that the maximum cure rates plotted in Figure 2 are due to two crosslinking reactions, one accelerated and one unaccelerated, and having means of measuring the rates of one of them and the combined rates of both of them, one can separate the maximum cure rates due to the two crosslinking reactions and examine them individually. By subtracting the maximum cure rates of the unaccelerated polymer from the

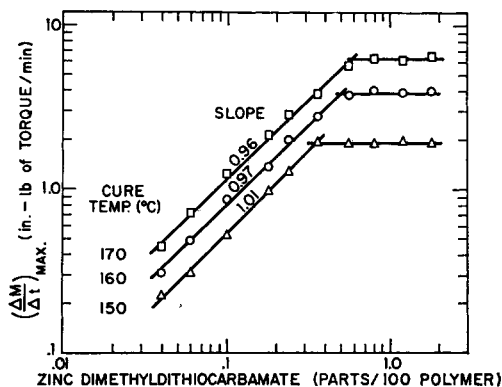


Fig. 5. Maximum cure rates vs. initial sulfur concentrations after subtraction of the maximum cure rates of the unaccelerated curing reaction. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5; ZnDMDC, as noted.

maximum cure rates of the ZnDMDC-accelerated polymer, we can isolate the maximum cure rates due solely to the ZnDMDC-accelerated curing reaction. These corrected maximum cure rates, due solely to the accelerated curing reaction, are plotted in Figure 5. The nearly unit slopes are in agreement with a first-order maximum cure rate with respect to initial ZnDMDC concentration.

### Cure Rate versus Cure Site Concentration

An important variable in the curing of EPDM elastomers is the amount of unsaturation present in the polymer. The cure rates of EPDM elastomers increase as the amounts of unsaturation in the polymers are increased. Since two cure sites are needed to form one crosslink, there is a reasonable probability that the rate of crosslinking is a function of the square of the amount of unsaturation. One method to determine quantitatively the relationship between cure rate and cure site concentration is to measure the cure rates of a number of EPDM polymers containing different amounts of unsaturation. This method is complicated by subtle variations in polymer composition, molecular weight, and structure which are difficult to detect and to control and which tend to obscure the effects of variations in polymer unsaturation content.



As polymers of varying unsaturation content but otherwise identical structures were not readily available, an alternative technique was employed to study the relationship of cure rate to cure site concentration. The EPDM elastomer was blended with varying amounts of EPM

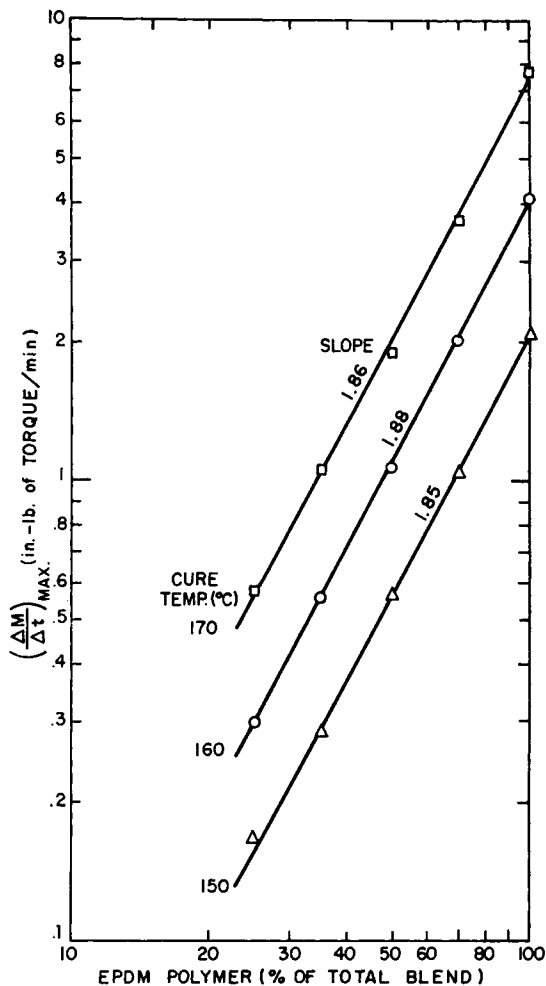


Fig. 6. Maximum cure rates vs. EPDM polymer concentrations for ZnDMDC-accelerated EPDM-EPM copolymer blends. Compounds: EPDM-EPM copolymer blend, 100; zinc oxide, 5; sulfur, 2; ZnDMDC, 1.6.

copolymer to produce a series of blends containing different amounts of unsaturation. The maximum cure rates of the blends were determined with the oscillating disk rheometer by using the same amounts of curing ingredients per hundred parts of each blend. Thus the initial concentration of cure sites was varied while the initial concentrations of the curing agents were held constant. A major unknown factor in the use of polymer

blends to relate cure rates to cure site concentrations is the kinetic effects of any macro- or microinhomogeneities present in the blends.

For EPDM-EPM copolymer blends containing ZnDMDC accelerator, the slopes of the lines relating maximum cure rates to EPDM polymer

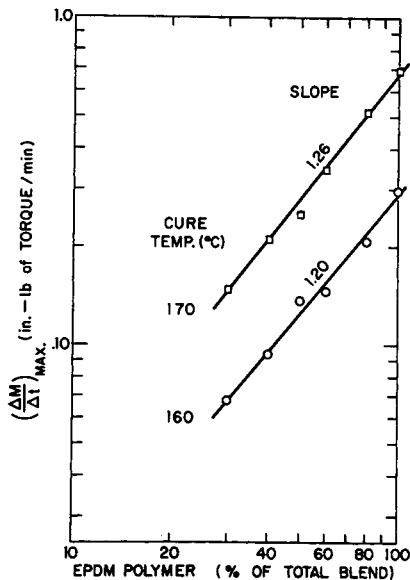


Fig. 7. Maximum cure rates vs. EPDM polymer concentrations for unaccelerated EPDM-EPM copolymer blends. Compounds: EPDM-EPM copolymer blend, 100; zinc oxide, 5; sulfur, 2.

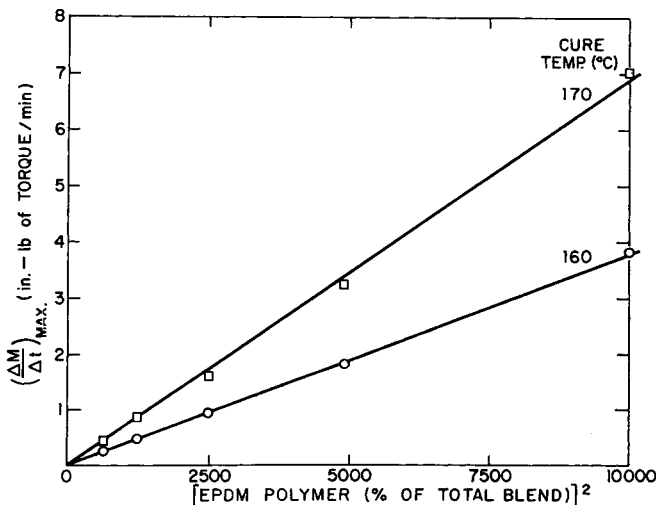


Fig. 8. Arithmetic plot of maximum cure rates vs. EPDM polymer concentrations squared for ZnDMDC-accelerated EPDM-EPM copolymer blends after subtraction of the maximum cure rates of the unaccelerated curing reaction. Compounds: EPDM-EPM copolymer blend, 100; zinc oxide, 5; sulfur, 2; ZnDMDC, 1.6.

concentrations in the blends vary from 1.85 to 1.88 at cure temperatures of 150–170°C., as shown in Figure 6. For unaccelerated EPDM–EPM blends containing only zinc oxide and sulfur, the slopes of the lines are of the order 1.2–1.3 as shown in Figure 7. When the maximum cure rates at

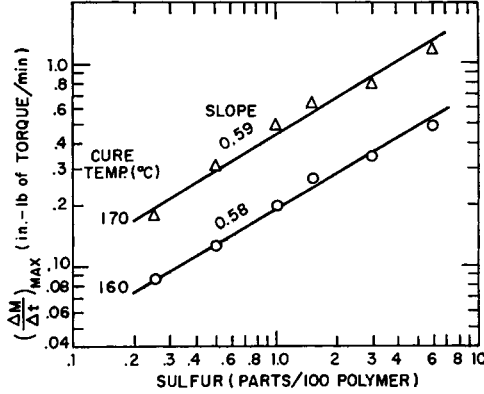


Fig. 9. Maximum cure rates versus initial sulfur concentrations for unaccelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, as noted.

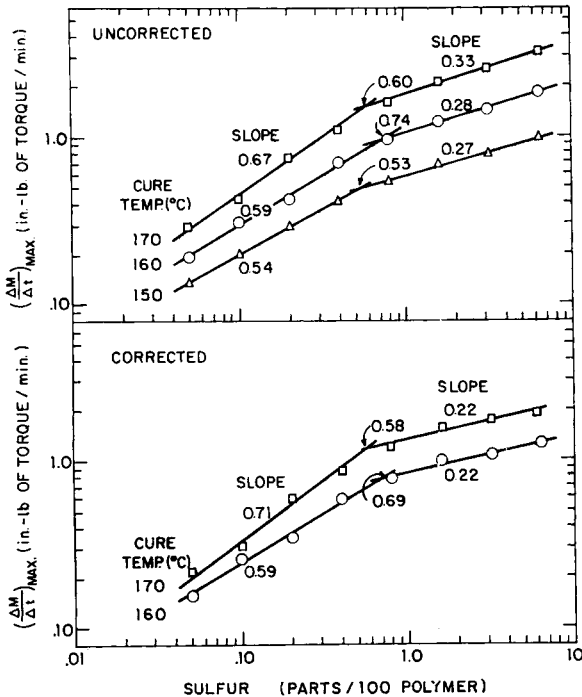


Fig. 10. Maximum cure rates vs. initial sulfur concentrations for EPDM polymer containing 0.1 part of ZnDMDC before and after correction by subtraction of the maximum cure rates of the unaccelerated curing reaction. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, as noted; ZnDMDC, 0.1.

160 and 170°C. of the ZnDMDC-accelerated blends are corrected for the contributions of the unaccelerated curing reaction and the corrected maximum cure rates are replotted versus the EPDM concentration, the resulting line slopes are increased slightly to 1.93–1.95. An arithmetic plot of the corrected maximum cure rates for the ZnDMDC-accelerated crosslinking reaction versus the square of the EPDM polymer concentration in the blends is linear with an intercept of zero as shown in Figure 8.

The results indicate that the maximum cure rates of the ZnDMDC-accelerated curing reaction are second-order in initial cure site concentration, while the maximum cure rates due to the unaccelerated curing reaction are 1.2 order in initial cure site concentration.

### Maximum Cure Rate versus Initial Sulfur Concentration

In the absence of ZnDMDC accelerator, the maximum cure rates of the EPDM polymer increase as the 0.6 power of the initial sulfur concentrations as shown in Figure 9. The rate of reaction of sulfur in unaccelerated natural rubber and butadiene–acrylonitrile compounds has been reported to be related to the 0.6 power of the sulfur concentration by Scheele.<sup>7</sup>

The dependence of the maximum cure rates on the initial sulfur concentrations for polymer containing 0.1 part of ZnDMDC is shown in Figure 10. The maximum cure rate data are shown before and after correction for the contributions from the unaccelerated crosslinking reaction. Correction of the data from the ZnDMDC-accelerated polymer for the contributions from the unaccelerated crosslinking reaction has only a minor effect on the slopes and intersections of the lines relating the maximum cure rates of the polymer to the initial sulfur concentrations.

EPDM polymer containing 1.5 parts of ZnDMDC (Fig. 11) has maximum cure rate versus initial sulfur concentration relationships similar

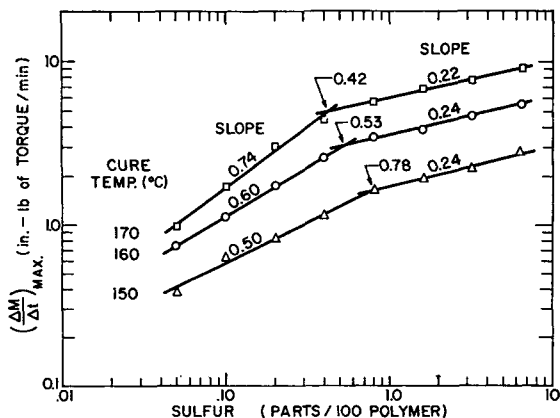


Fig. 11. Maximum cure rates vs. initial sulfur concentrations for EPDM polymer containing 1.5 parts of ZnDMDC. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, as noted; ZnDMDC, 1.5.

to those of polymer containing only 0.1 part of ZnDMDC (Fig. 10), indicating that these cure rate relationships are independent of accelerator concentration over this range. There is some indeterminacy in interpreting the results obtained with polymer containing 1.5 parts of ZnDMDC, as varying the initial sulfur concentration of the polymer would be expected to vary the solubility of ZnDMDC in the polymer. This is not a problem in polymer containing 0.1 part of ZnDMDC, as 0.1 part is well below the solubility limits of ZnDMDC at the curing temperatures involved.

### Maximum Cure Rate versus Initial Zinc Oxide Concentration

The maximum cure rates of EPDM polymer stocks containing no ZnDMDC accelerator are dependent upon the amount of zinc oxide in the polymer. Over the range 1–16 parts of zinc oxide, the maximum cure rates increase with increasing initial zinc oxide concentration as shown in Figure 12. The logarithmic relationships between the maximum cure rates and the initial zinc oxide concentrations are not linear, so no reaction orders were assigned. Zinc oxide acceleration of the reaction of sulfur with olefins has previously been observed by Bateman et al.,<sup>8</sup> who interpreted the phenomenon in terms of a polar mechanism for the sulfur-olefin reaction.

In comparison to the unaccelerated stocks, stocks containing ZnDMDC accelerator show relatively little acceleration of the maximum cure rate by increasing initial zinc oxide concentration in going from 1 to 16 parts of zinc oxide as shown in Figure 13. If the data for the ZnDMDC-accelerated stocks are corrected for the contributions of the unaccelerated curing reaction to the maximum cure rates and replotted as shown in Figure 13, there is, in general, a slight decrease in the maximum cure rates with increasing initial zinc oxide concentrations. The decrease in the maximum cure rates is of the order of magnitude of that which might be expected to occur due to the zinc oxide displacing polymer from the rheometer polymer sample.

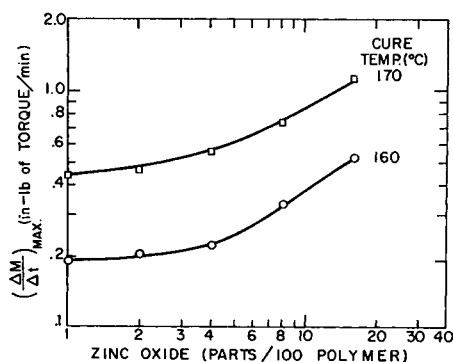


Fig. 12. Maximum cure rates vs. initial zinc oxide concentrations for unaccelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, as noted; sulfur, 1.5.

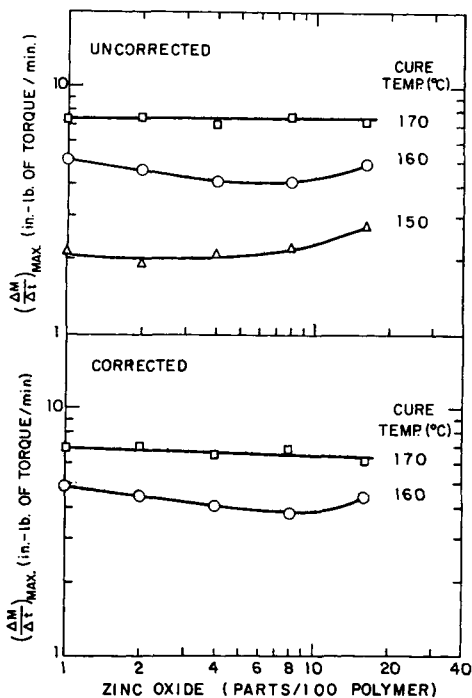


Fig. 13. Maximum cure rates vs. initial zinc oxide concentrations for ZnDMDC-accelerated EPDM polymer compounds before and after correction by subtraction of the maximum cure rates of the unaccelerated curing reaction. Compounds: EPDM polymer, 100; zinc oxide, as noted; sulfur, 1.5; ZnDMDC, 1.5.

## DISCUSSION

The kinetic data obtained on the curing of the ethylene-propylene-diene rubber have been interpreted to signify that two kinetically distinguishable crosslinking sequences are proceeding simultaneously during zinc dimethyldithiocarbamate accelerated cures. One of the crosslinking sequences is kinetically dependent on accelerator and the other is not. The crosslinking sequence which takes place in terpolymer which contains no accelerator has been found to have maximum cure rates which are 0.6 order in initial sulfur concentration, 1.2 order in initial cure site concentration, and of a positive variable order in initial zinc oxide concentration.

On the basis of our interpretation of the kinetic data to indicate that the unaccelerated crosslinking sequence can proceed simultaneously with the accelerator-dependent crosslinking sequence, the kinetic data obtained with zinc dimethyldithiocarbamate-accelerated stocks have been corrected by subtracting out the maximum cure rates of the unaccelerated crosslinking sequence. The corrected data indicate that for the accelerator-dependent crosslinking sequence the maximum cure rates are first-order in initial zinc dimethyldithiocarbamate concentration, second-order in initial cure site concentration, variable fractional order in initial sulfur concen-

tration, and approximately zero-order in initial zinc oxide concentration. The results also show that the maximum cure rates of the accelerated curing sequence are limited by the low solubility of zinc dimethyldithiocarbamate in the polymer.

No attempt has been made to interpret the kinetic data in terms of more detailed reaction mechanisms. It is considered that the data are not sufficiently limiting to narrow the choice to any one particular reaction mechanism from among the many which can be postulated to account for the complex chemistry of curing.

It is concluded on the basis of this study that the technique of correlating the maximum cure rates of gum elastomers as measured by using the Monsanto oscillating disk rheometer with the initial concentrations of the curing ingredients in the elastomers is a useful tool for gaining insight into the factors which control cure rates.

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