The Chemistry of Sulfur Curing.   Part II.   Kinetics of Vulcanization of an EPDM Elastomer Accelerated by Tetramethylthiuram Monosulfide and Disulfide*

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Synopsis

The induction periods and maximum cure rates of an EPDM gum rubber were determined by using the Monsanto oscillating disk rheometer and correlated against the initial concentrations of curing ingredients.   Sulfur curing systems accelerated by TMTM and TMTD were used.   The maximum cure rates of the TMTM-accelerated and the TMTD-accelerated EPDM terpolymer compounds differed significantly only at low sulfur concentrations where the TMTM-accelerated compounds had slower maximum cure rates.   Above approximately the 1% concentration level, TMTM and TMTD were found increasingly to retard the maximum cure rates of the EPDM terpolymer compounds as the initial concentrations of the thiuram accelerators were increased. The maximum cure rates of the TMTM- and TMTD-accelerated terpolymer compounds were found to be variable order in initial accelerator concentration, second-order in initial cure site concentration, approximately half-order in initial sulfur concentration above 0.3% sulfur, and of a positive variable order in initial zinc oxide concentration.

INTRODUCTION

The preceding paper in this series[1] dealt with the kinetics of the sulfur vulcanization of an ethylene–propylene–diene (EPDM) terpolymer elastomer which was either unaccelerated or accelerated with zinc dimethyl-dithiocarbamate (ZnDMDC).   The present paper is concerned with the kinetics of the sulfur vulcanization of an EPDM elastomer which is accelerated by either tetramethylthiuram monosulfide (TMTM) or by tetramethylthiuram disulfide (TMTD).

The same EPDM elastomer has been used in both studies, Nordel† 1070 hydrocarbon rubber which has been extensively extracted with acetone.   The kinetic studies were carried out on the gum terpolymer after addition of zinc oxide, sulfur, and accelerator.   The vulcanizations of the terpolymer compounds were followed with the aid of a Monsanto oscillating disk rheometer.   Analysis of the kinetic data was accomplished by relating

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† DuPont's registered trademark for its hydrocarbon rubber.

the induction times and the maximum cure rates of the terpolymer compounds to the initial concentrations of the components of the curing system.

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.

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

Tetramethylthiuram Monosulfide (TMTM). Thionex† rubber accelerator is sold by E. I. du Pont de Nemours and Company.

Tetramethylthiuram Disulfide (TMTD). Thiuram M is sold by E. I. du Pont de Nemours and Company.

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

Experimental Procedures

The procedures used are reported in the Experimental Section in the first paper in this series.[1]

RESULTS

Accelerator Effects

The relationships of maximum cure rate $\Delta M / \Delta t_{max}$ to initial accelerator concentration are quite similar for TMTD-accelerated and TMTM-accelerated EPDM terpolymer compounds (Fig. 1). At low accelerator concentrations the maximum cure rates of the terpolymer compounds increase rapidly with increased initial accelerator concentrations. At intermediate accelerator concentrations the increases in maximum cure rates with increased initial accelerator concentrations are more moderate. At high accelerator concentrations the maximum cure rates are actually decreased by increased initial accelerator concentrations. Correction of the maximum cure rate data from the thiuram-accelerated compounds for the cure rate contributions due to the unaccelerated sulfur crosslinking reaction does not result in any apparent simplification of maximum cure rate to initial accelerator concentration relationships (Fig. 2) as it did for the ZnDMDC-accelerated terpolymer compounds reported previously.[1]

Although TMTM-accelerated and TMTD-accelerated EPDM compounds have a similar dependence of maximum cure rate on initial accelerator concentration, the lengths of their induction periods differ as a

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* Registered trademark of Stauffer Chemical Company.
† Registered trademark of E. I. du Pont de Nemours & Co., Inc.
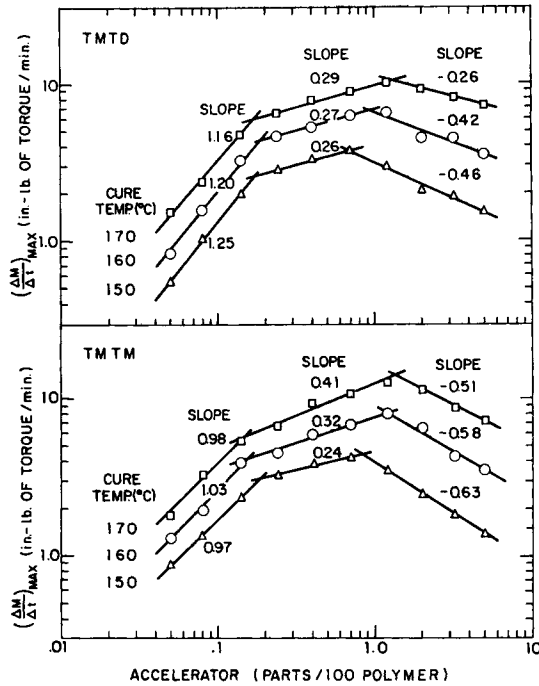‡ Registered trademark of New Jersey Zinc Company.

Fig. 1. Maximum cure rates vs. initial accelerator concentrations. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5; accelerator, as noted.
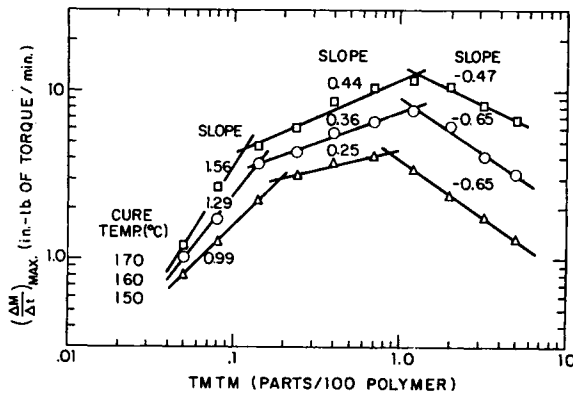

Fig. 2. Maximum cure rates vs. initial TMTM concentrations after subtraction of the maximum cure rates of the unaccelerated sulfur curing reaction. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5; TMTM, as noted.

function of accelerator structure and concentration. Stocks accelerated by TMTM have a somewhat longer induction period than stocks accelerated by TMTD. The TMTM-accelerated EPDM stocks show a significant decrease in the lengths of their induction period with increased initial accelerator concentration, whereas the TMTD-accelerated terpolymer com-
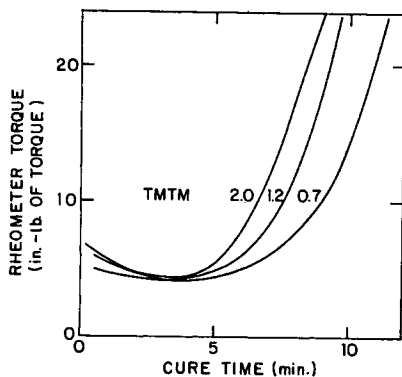
Fig. 3. Induction periods at 160°C. as a function of initial TMTM concentrations. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, 1.5; TMTM, as noted.

pounds show little decrease in the length of their induction period with increased accelerator concentration.

The dependence of induction time upon initial TMTM concentration is evident in Figure 3 from the shifts of the rheometer torque curves to the left with increasing TMTM concentration. Due to the frequently encountered difficulty of separating the effects due to induction time changes from those due to maximum cure rate changes, the relationships of induction time to curing system component have been treated on a qualitative rather than a quantitative basis. The induction time effects for the terpolymer stocks shown in Figure 3 are readily apparent as the stocks do not vary greatly in maximum cure rate.

It has been found that the lengths of the induction periods of the accelerated EPDM terpolymer compounds can be affected by variations in compounding technique. Prolonged milling of TMTM-accelerated terpolymer compounds has been observed to shorten the induction period of these compounds. Care was taken in this study to keep the compounding histories of the stocks as similar as possible.

Cure Site Effects

The dependence of maximum cure rate on initial cure site concentration was determined in this as in the previous study by use of EPDM terpolymer–EPM copolymer blends containing different proportions of EPDM terpolymer and thus different initial cure site concentrations. The EPDM terpolymer–EPM copolymer blend compounds when accelerated by either TMTM or TMTD were found to have a second-order dependence of maximum cure rate on initial cure site concentration identical to that found for the ZnDMDC-accelerated blends.[1] Typical results are shown in Figure 4 for TMTM-accelerated blends before and after correction for the cure rate contributions due to the unaccelerated crosslinking reaction. The second-order nature of the maximum cure rate dependence is indicated by the line slope values of 2.0 in the corrected logarithmic plot. Typical results for

TMTD-accelerated blends are shown in Figure 5 in the form of an arithmetic plot of the maximum cure rates after correction for the cure rate contributions due to the unaccelerated sulfur crosslinking reaction versus the squares of the EPDM terpolymer concentrations in the blends. The straight line arithmetic relationships which extrapolate to zero cure rate at zero terpolymer concentration are indicative of a second-order dependence
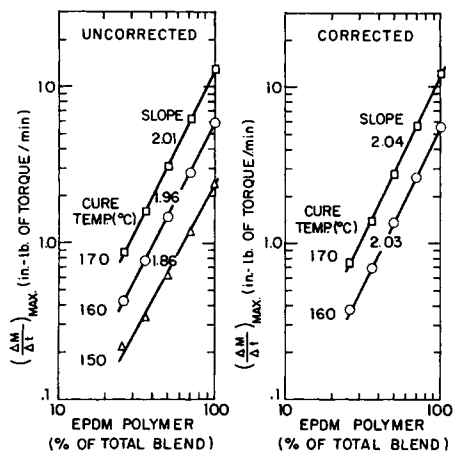

Fig. 4. Maximum cure rates vs. EPDM polymer concentrations for TMTM-accelerated EPDM–EPM polymer blends before and after correction for the maximum cure rates of the unaccelerated sulfur curing reaction. Compounds: EPDM–EPM polymer blends, 100; zinc oxide, 5; sulfur, 2.0; TMTM, 1.5.
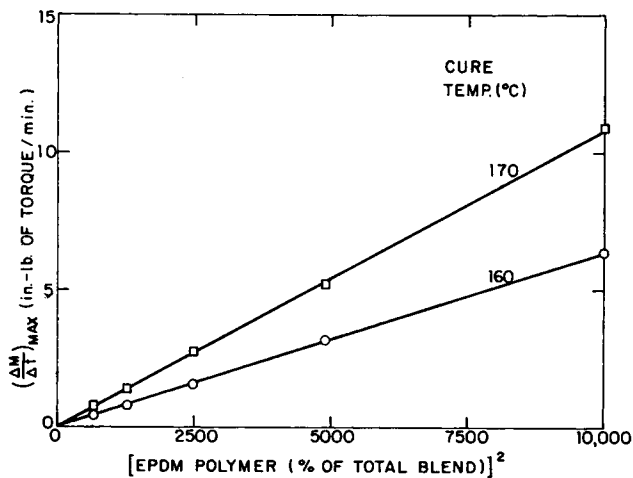

Fig. 5. Arithmetic plot of maximum cure rates after subtraction of the maximum cure rates of the unaccelerated sulfur curing reaction vs. EPDM polymer concentrations squared for TMTD-accelerated EPDM–EPM polymer blends. Compounds: EPDM–EPM polymer blends, 100; zinc oxide, 5; sulfur, 2.0; TMTD, 1.5.
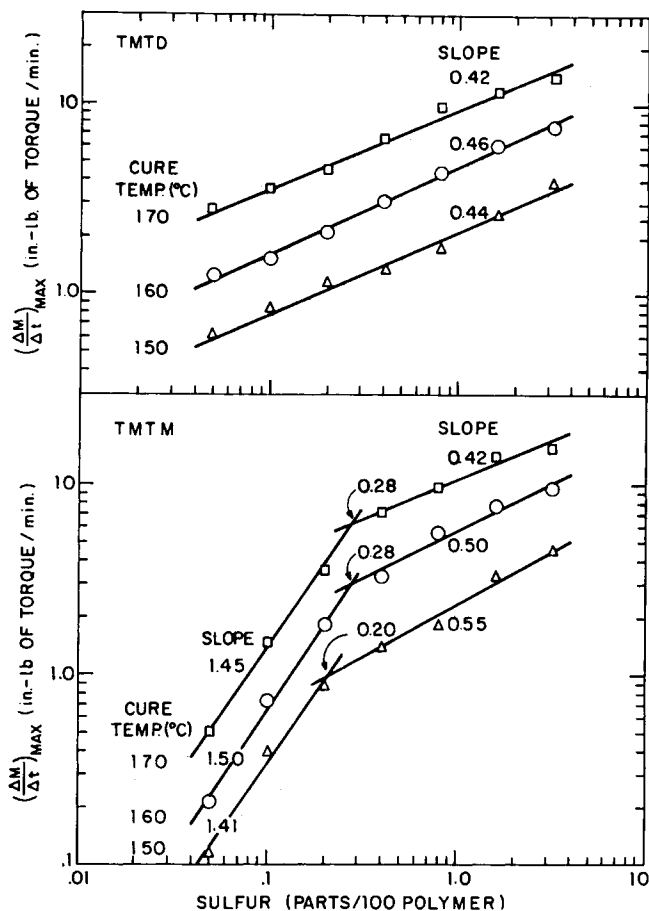
Fig. 6. Maximum cure rates vs. initial sulfur concentrations for TMTD- and TMTM-accelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, as noted; accelerator, 1.5.
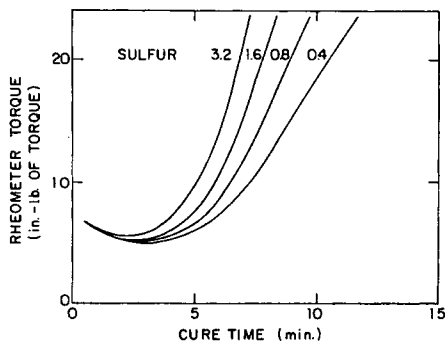

Fig. 7. Induction periods at 160°C. as a function of initial sulfur concentrations for TMTD-accelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, as noted; TMTD, 1.5.

of maximum cure rate on initial cure site concentration and of a lack of participation by the EPM copolymer in the crosslinking reaction.

The lengths of the induction periods of the EPDM–EPM blends decrease somewhat as the concentration of the EPDM terpolymer in the blends is increased. The effects of changing initial cure site concentration on the lengths of the induction periods are obscured somewhat by the large changes in cure rate brought about by the changes in the initial cure site concentration.

Sulfur Effects

The maximum cure rates of TMTM- and TMTD-accelerated EPDM terpolymer compounds increase as the initial concentrations of sulfur in the terpolymer compounds are increased (Fig. 6). For TMTD-accelerated compounds the maximum cure rates are proportional to the 0.4–0.5 power of the initial sulfur concentration. Correction of the maximum cure rate data for the cure rate contributions due to the unaccelerated sulfur crosslinking reaction has a negligible effect on the line slopes of Figure 6.

Terpolymer compounds accelerated by TMTM respond differently to changes in initial sulfur concentration than do those accelerated by TMTD. At low sulfur concentrations, the maximum cure rates of the TMTM-accelerated terpolymer compounds are significantly slower than those of the TMTD accelerated compounds. At about the 0.25 part sulfur level the maximum cure rates of the TMTM-accelerated terpolymer compounds catch up with those of the TMTD-accelerated compounds. Above this sulfur level the maximum cure rates of the TMTM- and the TMTD-accelerated compounds are nearly identical when compared on an equimolar concentration of accelerator basis. At the 0.23 part sulfur level in EPDM terpolymer containing 1.5 parts of TMTM accelerator, there is one atom of sulfur present for each molecule of TMTM accelerator present.

The initial sulfur concentration has a pronounced effect on the lengths of the induction periods of TMTM- and TMTD-accelerated EPDM stocks.
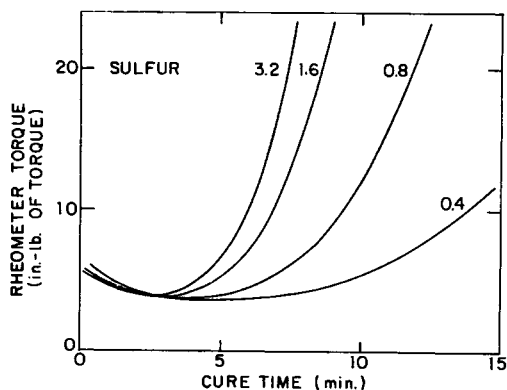

Fig. 8.   Induction periods at 160°C. as a function of initial sulfur concentrations for TMTM-accelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, 5; sulfur, as noted; TMTM, 1.5.

As shown in Figures 7 and 8, increasing the initial sulfur concentration shortens the induction period of the terpolymer stocks, particularly those accelerated by TMTM.

Zinc Oxide Effects

Increased initial zinc oxide concentrations result in increased maximum cure rates for TMTM- and TMTD-accelerated EPDM stocks both before and after correction of the data for the cure rate contributions from the unaccelerated sulfur crosslinking reaction (Fig. 9). The logarithmic plots of maximum cure rates versus initial zinc oxide concentrations have a curved line relationship so no reaction orders have been assigned. Increased initial zinc oxide concentrations also result in shorter induction
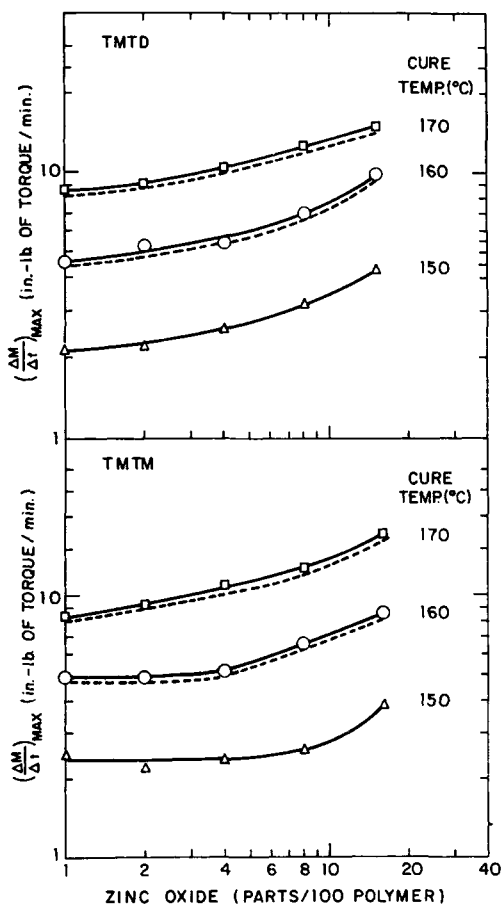
Fig. 9. Maximum cure rates vs. initial zinc oxide concentrations for TMTD- and TMTM accelerated EPDM polymer: (---) after subtraction of the maximum cure rates of the unaccelerated sulfur curing reaction. Compounds: EPDM polymer, 100; zinc oxide, as noted; sulfur, 1.5; accelerator, 1.5.
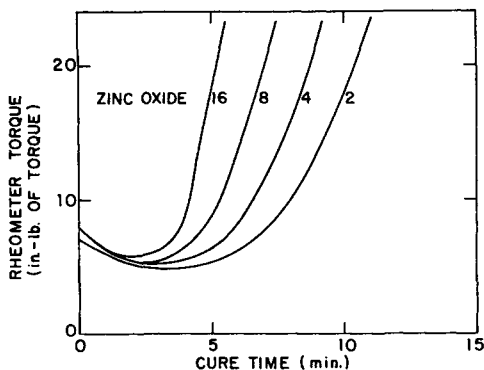
Fig. 10. Induction periods at 160°C. as a function of initial zinc oxide concentration for TMTD-accelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, as noted; sulfur, 1.5; TMTD, 1.5.
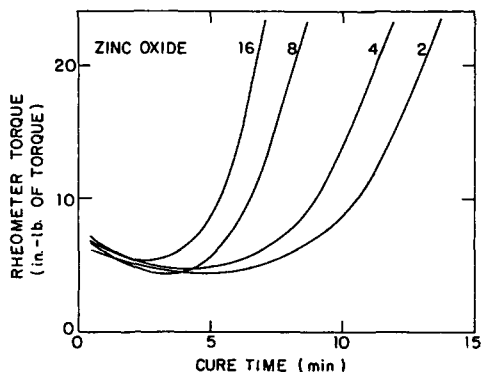

Fig. 11. Induction periods at 160°C. as a function of initial zinc oxide concentration for TMTM-accelerated EPDM polymer. Compounds: EPDM polymer, 100; zinc oxide, as noted; sulfur, 1.5; TMTM, 1.5.

periods for the TMTM- and TMTD-accelerated terpolymer compounds (Figs. 10 and 11).

DISCUSSION

The vulcanization kinetics of the thiuram monosulfide-accelerated ethylene–propylene–hexadiene terpolymer compounds are quite similar to those of the thiuram disulfide-accelerated compounds. This is not surprising in view of the relative ease with which the monosulfide compound is converted to the disulfide by reaction with sulfur.[2] It seems probable that the monosulfide reaction with sulfur is responsible for the major difference in cure rates between the monosulfide and disulfide systems which occurs at low sulfur concentrations. If the monosulfide has little or no accelerating ability until it has reacted with sulfur to form thiuram disulfide or thiuram disulfide derivatives, low sulfur concentrations could slow this step of the

process and thus affect the overall curing kinetics. Alternatively, at low sulfur concentrations, the thiuram monosulfide–sulfur reaction could starve the total curing system for sulfur. Since the maximum cure rates of thiuram disulfide-accelerated compounds are proportional to the 0.4–0.5 power of the initial sulfur concentration, the maximum cure rates for the system would be expected to be lower by the extent that the ambient sulfur concentration is reduced.

Even though the tetramethylthiuram monosulfide and disulfide accelerators are converted to zinc dimethyldithiocarbamate during vulcanization of the terpolymer,[3] it is possible to obtain faster maximum cure rates for the ethylene–propylene–diene terpolymer through use of the thiuram accelerators than by use of zinc dimethyldithiocarbamate accelerator. This is due to the low solubility of the zinc salt in the polymer. It would appear that the thiuram accelerators promote a considerable amount of crosslinking before they are converted to zinc dimethyldithiocarbamate, otherwise they would be unlikely to yield faster maximum cure rates. This raises the possibility that the thiuram compounds may be accelerating different types of curing reactions than is the zinc dimethyldithiocarbamate.

The discovery that the thiuram vulcanization accelerators also act as vulcanization retarders at higher concentrations was unexpected. Analogous behavior has been noted previously in the polymerization of methyl methacrylate. Tetramethylthiuram disulfide was found to act both as an initiator and as a retarder of methyl methacrylate polymerization.[4] This dualistic behavior results in the rate of the radical polymerization passing through a maximum with increasing tetramethylthiuram disulfide concentration similar to the maximum found in the rate of vulcanization of the EPDM terpolymer compound with increasing initial tetramethylthiuram disulfide concentration. This similarity in kinetic behavior of the polymerization and vulcanization reactions might be taken as evidence that the vulcanization reaction proceeds via a free-radical mechanism. On the other hand, the shortened induction periods and increased cure rates brought about by increased initial zinc oxide concentrations might be ascribed to polar reactions as has been done previously for model vulcanization reactions of 2,6-dimethylocta-2,6-diene.[5] Further studies are in progress directed toward elucidating in detail the mechanisms of the vulcanization reactions.

References

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