

Structural Characterization of Vulcanizates. XII. Efficient Vulcanization Using a Sulfenamide- Thiuram Disulfide Accelerator System

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Synopsis

Vulcanizates obtained from the sulfur vulcanization of natural rubber using a combination of the accelerators N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and tetramethylthiuram disulfide (TMTD) have been analyzed in terms of the numbers of poly-, di-, and monosulfide crosslinks, network-bound accelerator residues, and cyclic sulfide chain modifications as a function of cure time. The vulcanization system produced mainly monosulfide crosslinks at optimum cure, although there were differences in detail between this mixed system and a previously reported efficient sulfur vulcanization (EV) system using a high ratio of CBS to sulfur.

INTRODUCTION

Efficient sulfur vulcanization (EV) of natural rubber (NR), i.e., vulcanization which produces mainly monosulfide crosslinks and relatively few noncrosslinking modifications of the main chains, offers improvements in thermal and thermal-oxidative aging over conventional vulcanization.¹ The increased efficiency of vulcanization can be achieved in a number of ways,¹ most of which involve an increase in the ratio of total organic accelerator to elemental sulfur. Part XI of this series² presented a detailed structural characterization of an EV system produced using a very high ratio (15:1 by wt) of N-cyclohexylbenzothiazole-2-sulfenamide (CBS) to sulfur. For a number of reasons (technical and economic) this vulcanization system is not commercially attractive; but Skinner and Watson¹ showed that similar overall efficiencies could be obtained using a sulfenamide or similar accelerator in conjunction with an ultra-accelerator (e.g., tetramethylthiuram disulfide, TMTD) at a much lower total accelerator-to-sulfur ratio. A limited amount of data has already been published on the chemical structure of some of these mixed accelerator EV systems,^{1,3} but the present work was undertaken with the particular aim of determining whether the mixed accelerator systems result in formation of the same high level of network-bound accelerator residues (pendent groups) as does the CBS-sulfur EV system.² A mixed accelerator system containing CBS (1.44 phr) and TMTD (0.66 phr) was chosen for study.

In addition to the characterization of crosslink types as a function of cure time, the amounts of each accelerator which became bound to the network were determined by preparing and analyzing samples in duplicate, once using radioactive CBS and nonactive TMTD and again using nonactive CBS and radioactive TMTD.

EXPERIMENTAL

Preparation of ^{14}C -Labeled TMTD

Carbon 14-labeled TMTD was prepared by a modification of the method of Rothstein and Binovic.⁴ ^{14}C -Carbon disulfide (0.2 mC) was diluted with freshly distilled unlabeled carbon disulfide (1.00 g) and distilled into dioxan (10 ml) in vacuo. The solution was added dropwise to a solution of dimethylamine (13.25 mM) in aqueous sodium carbonate (40%, 1.3 ml), and the mixture was shaken at room temperature for 1 hr. A solution of potassium ferricyanide (4.36 g) in water (13 ml) was added slowly and the resultant white precipitate was collected, washed with water and cold ethanol, and dried in vacuo (0.933 g, 65%, mp 150–2°C, lit.⁴ 151°C). The total activity of the product was 0.115 mC (4581 d/sec/mg), representing an overall radiochemical yield of 58%. Radiochemical purity, as determined by isotope dilution analysis, was 107%.

^{14}C -Labeled CBS was the same material as used in earlier work.² The activity was 2115 d/sec/mg.

Preparation and Analysis of Vulcanizates

The vulcanization recipe was NR (RSS1, yellow circle; 100); sulfur (sieved flowers; 0.35), CBS (recrystallized; 1.44), TMTD (recrystallized; 0.66), zinc oxide (Gold Seal; 5.0), and lauric acid (2.0). The radioactive accelerators were incorporated in the mixes by the procedure described in part XI.² Two sets of vulcanizates were prepared as 1-mm-thick sheets at 140°C for cure times of 20, 30, 40, 60, 120, and 360 min. One set (series A) contained radioactive CBS and nonactive TMTD; the other set (series B) contained nonactive CBS and radioactive TMTD. A third set of vulcanizates (series C), with cure times of 20, 40, and 360 min, was prepared from nonactive accelerators and used for combined sulfur analysis.

Chemical crosslink densities were obtained via stress-strain measurements on dry vulcanizate samples by previously described procedures,^{5,6} with the assumption that chain scission was zero throughout the vulcanization period. Analyses of the distribution of crosslink types was carried out using propane-2-thiol and *n*-hexanethiol chemical-probe reagents.^{5,7} The former reagent was previously shown to give cleavage of both polysulfide and disulfide pendent accelerator residues.² Efficiency parameters E (atoms of sulfur combined in the network per crosslink) and E' (atoms of sulfur combined in the network per crosslink originally present, after treatment with triphenylphosphine, PPh_3) were derived by the procedures described by Saville and Watson.⁸

Vulcanizate activities were obtained by the combustion analysis procedure previously described.² Extraction of nonbound accelerator residues from the ¹⁴C-CBS vulcanizates was by the acetic acid/acetone-chloroform-methanol azeotrope sequence previously described.² Extraction of the nonbound TMTD residues from the ¹⁴C-TMTD vulcanizates was with cold methylene dichloride for 96 hr under nitrogen.⁹

RESULTS AND DISCUSSION

Table I gives the total concentration of radioactive accelerator (or products derived from the 2-benzothiazolylthio- or dimethyldithiocarbamyl residues) in the two sets of radioactive vulcanizates and in the corresponding uncured mixes as measured by combustion analysis, together with the concentrations calculated on the basis of the weights of accelerators used. The discrepancy between the calculated and observed concentrations in series A was of the same magnitude as that observed in the earlier work with ¹⁴C-CBS at comparable accelerator level.² Series B showed good agreement between the calculated and observed concentrations in the mix, but there was a continuous drop in the measured concentration with cure

TABLE I
Total Accelerator in Unextracted Vulcanizates

| Cure time, min | Moles of accelerator/g RH, $\times 10^6$ | |
|------------------|--|-----------------------|
| | Series A ^a | Series B ^b |
| 20 | 5.07 | 4.78 |
| 30 | 5.19 | 4.62 |
| 40 | 4.98 | 4.40 |
| 60 | 5.11 | 4.36 |
| 120 | 5.05 | 4.07 |
| 360 | 4.97 | 3.30 |
| Mix | 4.97 | 5.50 |
| Calculated value | 5.58 | 5.63 |

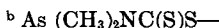
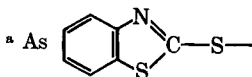


TABLE II
Efficiency Parameters for Vulcanizate of Series C

| Cure time, min | 10^5 (2 Mc, chem) ⁻¹ , moles/g RH | Network combined sulfur, g atoms/g RH, $\times 10^4$ | | E^a | E'^a |
|----------------|--|--|----------------------------------|-------|--------|
| | | Before PPh ₃ treatment | After PPh ₃ treatment | | |
| 20 | 2.75 | 1.32 | 0.60 | 4.8 | 2.1 |
| 40 | 3.05 | 0.96 | 0.83 | 3.1 | 2.7 |
| 360 | 2.40 | 0.89 | 0.89 | 3.7 | 3.7 |

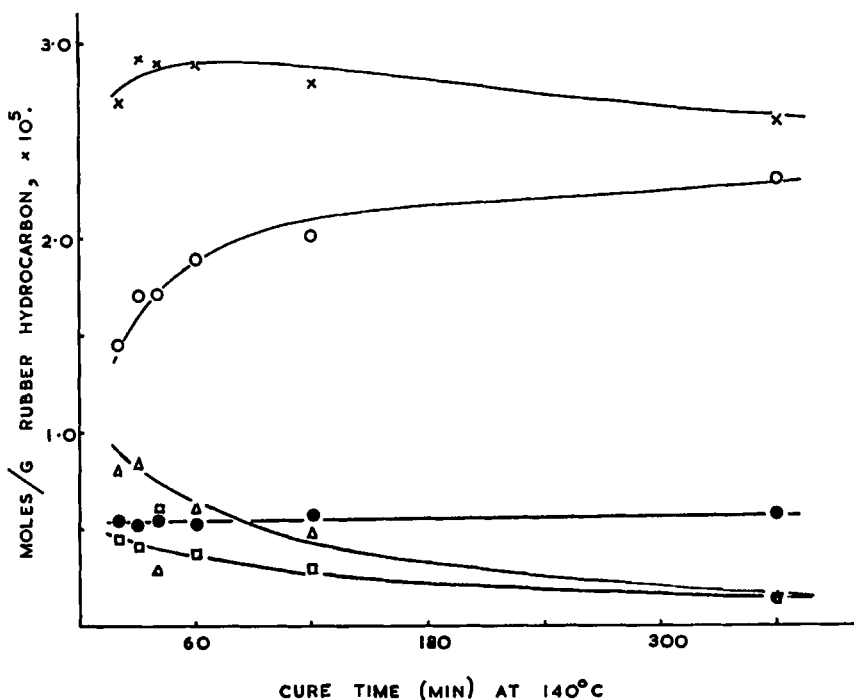


Fig. 1. Distribution of crosslink types and pendent benzothiazole groups as a function of cure time at 140°C for the vulcanization system RSS1 (100), S (0.35), CBS (1.44), TMTD (0.66), ZnO (5.0), and lauric acid (2.0). Series A: (x) total crosslinks; (o) monosulfide crosslinks; (Δ) disulfide crosslinks; (□) polysulfide crosslinks; (●) total benzothiazole pendent groups.

time. This was most probably a reflection of thermal decomposition of TMTD and its vulcanization reaction products to carbon disulfide, which was lost from the network prior to combustion analysis.

The results of crosslink distribution analysis and pendent group analysis are summarized in Figures 1 and 2 for vulcanizate series A and B, respectively. The two series did not produce vulcanizates of identical total crosslink density. The difference was associated with a somewhat lower rate of disappearance of di- and polysulfide crosslinks in series A, and would appear to be due to slightly greater opportunities for thermal decomposition of polysulfide crosslinks relative to desulfuration to form monosulfide crosslinks. These differences in cure behavior may have arisen from small differences in the purities of the radioactive and nonradioactive accelerator samples. At a cure time of 60 min (approximately optimum cure) the monosulfide crosslinks constituted 65% of the total crosslinks. This compares with a figure of 81% found for the CBS/sulfur EV system² and a figure of 100% reported by Farlie³ for the combination TMTD/2-(4-morpholinylmercapto)benzothiazole (0.66:1.40 w/w). The degree of efficiency of the present system (as measured by the rate and extent of forma-

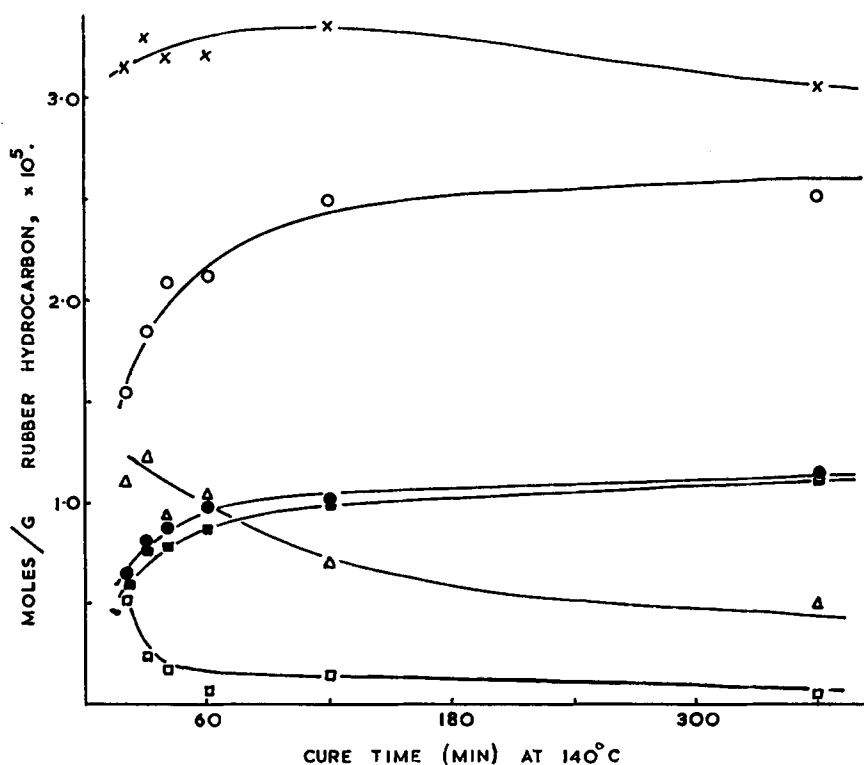


Fig. 2. Distribution of crosslink types and pendent dimethyldithiocarbamyl groups as a function of cure time at 140°C for the vulcanization system RSS1 (100), S (0.35), CBS (1.44), TMTD (0.66), ZnO (5.0), and lauric acid (2.0). Series B: (x) total crosslinks; (o) monosulfide crosslinks; (Δ) disulfide crosslinks; (\square) polysulfide crosslinks; (\bullet) total dimethyldithiocarbamyl pendent groups; (\blacksquare) monosulfidic dimethyldithiocarbamyl pendent groups.

tion of monosulfide crosslinks) was therefore somewhat less than that of the other two EV systems.

The total number of pendent groups derived from the CBS accelerator (series A, Fig. 1) remained essentially constant over the entire range of cure times studied. These pendent groups were not reactive toward propane-2-thiol and piperidine in heptane solution² and were therefore monosulfidic in character. At a cure time of 60 min, the concentration of these pendent groups was 19% of the total chemical crosslink concentration, and represented 11% of the CBS accelerator present in the mix. The proportion of the added CBS which became bound to the network was the same as was found for all three of the series of CBS vulcanizates studied previously.²

The total number of network-bound dimethyldithiocarbamyl residues derived from the TMTD accelerator (series B) increased with cure time up to 60 min and then remained relatively constant (Fig. 2). There were a small number of di- or polysulfide pendent groups (reactive toward pro-

pane-2-thiol and piperidine in heptane solution) at early cure times, but these disappeared entirely after 60 min of cure. It is of interest that the very mild extraction conditions to which the vulcanizates of series B were subjected failed to reveal the presence of substantial numbers of poly- or disulfide pendent groups. A major problem in the earlier work with CBS vulcanizates² was the development of extraction conditions which would efficiently remove the zinc salt of 2-mercaptobenzothiazole, and there was a certain amount of doubt as to whether the polysulfide pendent groups survived the conditions which were finally employed. At a cure time of 60 min, the total number of network-bound dimethyldithiocarbamoyl residues was 33% of the total chemical crosslink concentration, and the proportion of the original accelerator which was bound to the network was 19% (based on the measured amount of accelerator in the mix).

Combining the results for series A and B, the total number of network-bound accelerator residues at a cure time of 60 min was 52% of the total number of chemical crosslinks. When this result is considered in conjunction with the value of 2.7 found for the efficiency parameter E' (at 40 min cure, Table II), it follows that the number of cyclic sulfide modifications of the main chains is approximately the same as the number of pendent groups.* Viewed in this light, the TMTD/CBS EV system is slightly more efficient than the CBS EV system; i.e., there are slightly fewer pendent groups and cyclic sulfides.

* For this estimation it must be remembered that each pendent group contains two sulfur atoms. The pendent groups therefore account for approximately one atom of sulfur present in the network for each chemical crosslink. Since $E' - 1$ represents the total number of sulfur atoms combined in the network in structures other than crosslinks, there must be approximately 0.7 atoms of sulfur present as cyclic sulfides, i.e., there are approximately half as many cyclic sulfides as there are crosslinks.

References

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