

Study of Curative Interactions in *cis*-1,4-Polyisoprene (IR). V. General Experimental Procedure

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SYNOPSIS

The tetramethylthiuram disulfide (TMTD) and zinc dimethyldithiocarbamate (ZDMC) related vulcanization of *cis*-1,4-polyisoprene (IR) were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and electron spin resonance (ESR). The progress of the reactions in a given compound was monitored by analyzing the vulcanizate at selected points along the DSC curing curve. Full details of the analysis procedures are given. Analysis were mainly concerned with measurement of the crosslink densities, percentage of polysulfidic crosslinks, and the types and quantities of extractable compounds by thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC).

INTRODUCTION

Following on a study of the interactions of curatives such as sulfur, tetramethylthiuram monosulphide (TMTM), tetramethylthiuram disulphide (TMTD), stearic acid, zinc stearate, ZnO, and ZnS in the absence of rubber,¹⁻³ a detailed study was made of reactions of these curatives in synthetic *cis*-1,4-polyisoprene (IR). Use was made of DSC, TGA, and ESR in direct measurements, supplemented by the determination of crosslink densities and type of sulfidic bonds. This study reviews analysis methods for extractable compounds that were available in the literature. It describes modifications to some of these experimental techniques and outlines contemporary procedures with TLC and HPLC that were followed in our study to ascertain the amounts of curatives, intermediates, and reaction products.

Literature Methods for the Analysis of Vulcanizate Extracts

Several analytical techniques have been suggested to determine chemical species in vulcanizate extracts.

Tetramethylthiourea (TMTU)

Craig et al.^{4,5} isolated TMTU from vulcanizates with a short-path distillation technique. Moore et al.⁶ separated TMTU by sublimation at 60°C *in vacuo* and determined the quantity thereof by complex formation with mercury(II) nitrate. The latter method could only be applied to vulcanizates devoid of TMTD.

TMTM and TMTD

Craig et al.^{4,5} used a short-path distillation technique to isolate TMTM and TMTD, while Scheele et al.⁷ investigated the conductometric titration of TMTM with copper sulfate and found that the results fluctuated considerably.

Moore et al.⁶ determined TMTD in IR-TMTD-ZnO extracts by reacting it with an excess of thiosulfate ions in the presence of zinc ions. The resultant zinc dimethyldithiocarbamate (ZDMC) was removed by solvent extraction, and the remaining thiosulfate titrated with iodine to determine the amount of TMTD. In control experiments, determinations of standard solutions of TMTD (40–100 mg) in the presence of ZDMC (50–250 mg) and TMTU (20–80 mg) were accurate within ±1%.

Scheele et al.⁷ reported on the conductometric titration of TMTD with copper sulfate in the pres-

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ence of hydroquinine. Concentrations as low as ~ 20 ppm could be determined with a deviation of -2% from the theoretical, though in the presence of zinc dithiocarbamates deviations increased.

ZDMC

Craig et al.^{4,5} determined the amount of ZDMC in NR-ZDMC blends by distillation, but only 62.5 mol % ZDMC was recovered. Moore et al.⁶ digested ZDMC in vulcanizate extracts with a glacial acetic acid-hydrochloric acid mixture. The zinc ions were titrated with the disodium salt of diaminoethane-tetraacetic acid using Solochrome Black indicator. Another method of Moore et al.⁶ relied on the conversion ZDMC to copper(II) dimethyldithiocarbamate (CuDMC), after which the concentration was determined with colorimetry. Neither TMTD nor TMTU interfered with the analysis. However, the influence of the yellow compound TMTM, which does form in IR-TMTD-ZnO vulcanization systems (see later publication in this series) was not taken into account.

Kaniwa⁸ determined the concentration of ZDMC in vulcanizates with reversed-phase high-performance liquid chromatography. A key step in this approach was to convert the labile ZDMC complex to its much more inert cobalt analog prior to analysis. This step was essential as it has been reported⁹ that ZDMC-containing solutions gave no peak on performing the HPLC analysis.

Elemental Sulfur

An ASTM method¹⁰ used strontium chloride in the presence of sodium sulfite to oxidize sulfur to thio-sulfate, which was then determined iodometrically with starch as indicator (standard deviation 15–20%). Puacz¹¹ suggested the determination of traces of sulfur in rubber extracts by cleavage of the S₈ ring with sodium borohydride. The products were precipitated as mercury(II) sulfide, and the excess of mercury(II) ions reduced with tin(II) chloride. The concentration of the metallic mercury was determined with flameless cold vapor atomic absorption spectrometry (standard deviation 1.9%).

Recently King et al.¹² reported on the easy determination of elemental sulfur with HPLC (standard deviation 0.21%, detection limit 0.5 ppm). A TSK type H gel permeation column (Supelco, 300 \times 7.5 mm ID) was used.

EXPERIMENTAL

Instrumentation

Calorimetric investigations were conducted with a Du Pont 910 DSC module, connected to a Du Pont 9000 thermal analyzer. The temperature calibration was performed with indium and zinc, and the energy calibration with indium. The mass loss experiments were carried out with a Du Pont 951 TGA module. In both DSC and TGA experiments high-purity nitrogen was used as a purge gas (20 mL/min). The temperature calibration of the TGA was synchronized with that of the Du Pont DSC by means of the dehydration pattern of copper sulfate pentahydrate.

A Waters HPLC system, comprising a WISP 712 automatic injector, a Model 510 pump, and a Model Lambda-Max 481 variable wavelength detector, was used for the quantitative determination of extractable materials. The products were separated with a μ -Bondapack RPC-18 column (Waters, 300 \times 4 mm ID, particle size 10 μ m). The detection wavelength of 280 nm was preferred to prevent possible interference by minute amounts of benzene.

Ultraviolet spectra were recorded with a Shimadzu UV-3100 spectrophotometer. The ESR studies were conducted with a Varian E-9 spectrometer, equipped with 100-kHz modulation and a X-band klystron.

Materials

The materials used (as is) in the investigation were IR (IR 80, Karbochem, SA); poly(ethylene-co-propylene) (EPM) (EP 048, Carst and Walker, SA); sulfur (fumigation sulfur, chemical purity 99.5%, AECI, SA); TMTD (Orac TMTD, chemical purity 97%, Orchem, SA); TMTM (Vulkacit Thiuram MS, chemical purity 97.9%, Bayer, GFR); TMTU (chemical purity 98%, Aldrich Chemicals, USA); ZDMC (Vulkacit L, zinc content 22.8%, free amine content 0.04%, Bayer, GFR); stearic acid (iodine value 8.0 Wijs, Marine Oil Refiners, SA); zinc stearate (typical free fatty acid content 5%, Cookson Chemicals, SA); ZnO (active grade, chemical purity 99.72%, particle size less than 0.2 μ m, Zinc Process, SA); ZnS (chemical purity 99.99%, Aldrich Chemicals, USA); Cobalt(II) chloride (chemical purity 97%, Hopkin and Williams, UK); benzene (chem-

ical purity 99.8%, Holpro, SA); methanol (chemical purity 99.8%, Holpro, SA).

General Description

Samples were vulcanized in the DSC and the progress of the reaction monitored by stopping the reaction at selected points on the DSC curing curve. The crosslink density, type of crosslinks, and the composition of the extra-network material were then determined as outlined later. A key factor in our approach, which differed from those reported in the literature, was to use higher than normal curative loadings, thereby increasing the DSC signal. A potential drawback of using higher curative loadings, however, is that reactions that do not normally play a major role in vulcanization could become important in, for example, bimolecular processes.

The notation to identify the compounds prepared was of the typical form: IR (100)/TMTD (8.86)/ZnO (3.00) (1.0/1.0 mol ratio). This meant that TMTD (8.86 phr) and ZnO (3.00 phr) were mixed in a one mole equivalent with respect to each other, with IR. The initial concentration of each curative was 33.5×10^{-5} mol/mL elastomer.

The Mixing Procedure

The compounds were prepared in a Brabender Plasticorder with a type W30 mixing head of a 30-mL capacity, using a fill factor of 0.8. The temperature was maintained below 45°C to prevent premature interaction between curatives themselves and curatives with IR.

The elastomer was masticated for 6 min at 40 rpm, after which vulcanization ingredients were added. Blending was continued for a further 6 min at 30 rpm. The EPM-based mixtures were prepared in exactly the same way, except that the mixing head was heated to 92°C to permit blending.

DSC Experiments

Samples (~ 17 mg) were weighed on a microbalance, compressed in the DSC pans, and encapsulated. The pans did not seal well enough to prevent the escape of volatiles during a run.

Heating rates of 2.5°C/min were used, except where noted otherwise. At the desired temperature the sample was taken out of the DSC and the reactions quenched by cooling the sample in liquid nitrogen. Samples were reweighed after each DSC run.

Determination of the Crosslink Densities and Percentage Polysulfidic Crosslinks

The vulcanizates were extracted with a 0.1 m/m% solution of the stabilizer *N*-phenyl-1-naphtylamine (PAN) in benzene. The samples were immersed in the benzene-PAN (2.0 mL) solution in a specimen bottle and kept for 24 h in the dark, after which the solvent was renewed and the extraction continued for another 24 h at room temperature. The swollen sample was lightly dried with a paper towel and sealed in an alumina foil tube before weighing. The sample was allowed to deswell in a fume cupboard and subjected to high vacuum (13.3 Pa) for 48 h in the dark. The residual mass was determined, and the equilibrium value of V_r (volume fraction of the rubber network in the swollen gel) calculated (relative standard deviation 3.0%). The crosslink density ($\frac{1}{2} M_c$) was calculated using the Flory-Rehner¹³ equation.

The percentage of polysulfidic crosslinks was determined with a 0.4 *M* propane-2-thiol-piperidine chemical probe in *n*-pentane, which cleaves di(2-alkenyl) polysulfidic crosslinks.¹⁴ Samples were kept under nitrogen in the dark, and the reaction was shown to occur quantitatively in 2 h.

Analysis of Extractable Curatives and Intermediates

Most of the analytical methods reviewed earlier, were unsuitable in the current study, as the vulcanizates weighed only ~ 17 mg. Analysis were conducted with TLC and HPLC; and though limited success was obtained with adsorption HPLC, reversed-phase HPLC gave excellent separation between compounds.

TLC Analysis. The benzene extracts were concentrated to a total volume of 2.0 mL. A 10.0- μ L aliquot was applied to the TLC plate, and the procedure described earlier² followed. PAN did not interfere with these analysis.

HPLC Analysis. The benzene extracts were evaporated, and the residue redissolved in methanol and a minimum amount of methylene chloride, filtered through cotton wool, and diluted to 25.0 mL with methanol. This solution will be referred to as the sample master solution.

1. **TMTU, TMTM, and TMTD.** From a stock solution containing TMTU, TMTM, and TMTD (100 ppm), standard solutions of 20, 10, and 4 ppm were prepared. Aliquots of 20 μ L were analyzed at

a flow rate of 1.0 mL/min, using a methanol-H₂O (1/1, v/v) mixture as elutriant. The compounds eluted in the order TMTU ($t_R = 4.12$ min), TMTM ($t_R = 4.95$ min), and TMTD ($t_R = 6.66$ min). The sharp peaks did not overlap, and the calibration curves were virtually linear. The UV spectra of these compounds in methanol revealed ϵ_{280} for TMTU, TMTM and TMTD to be 1966, 11,434, and 11,497 I/mol cm⁻¹, respectively. (The abbreviation t_R refers to the retention time, and ϵ_λ is the molar absorptivity at a particular wavelength.)

A 5.0-mL aliquot of the sample master solution was diluted to 10.0 mL in a volumetric flask and analysed as before. The other compounds in the sample solution, such as PAN, ZDMC, sulfur, and minute amounts of benzene, did not interfere with the analysis.

2. ZDMC. The method of Kaniwa⁸ was used, but methanol instead of dichloromethane served as the solvent. A stock solution of cobalt (III) dimethyldithiocarbamate (CoDMC) was prepared by pipetting 46.7 mL of 250 ppm cobalt (II) chloride in methanol into 10 mg of ZDMC suspended in 30 mL methanol in a 100.0-mL volumetric flask. The ZDMC-cobalt (II) chloride (1.0/1.5 mol ratio) mixture reacted instantly to form CoDMC, which gave a characteristic green color in methanol. The flask was filled to the calibration mark with methanol, and standard solutions containing 40, 20, and 10 ppm zinc ions were prepared from the stock solution. The UV spectrum of CoDMC prepared via this route corresponded with that reported in the literature,⁸ and an ϵ_{280} value of 31,429 I/mol cm⁻¹ was calculated. The column was conditioned by prior injection with 50 μ L of 250 ppm cobalt (II) chloride in methanol. Aliquots of 20 μ L were analyzed at a flow rate of 1.0 mL/min, using a methanol-H₂O (6/4, v/v) mixture as elutriant. CoDMC ($t_R = 6.40$ min) eluted as a sharp symmetrical peak, and the calibration curve was linear.

A 5.0-mL aliquot of the sample master solution was pipetted into a 10.0-mL volumetric flask, and 1.5 mL of 250 ppm cobalt (II) chloride in methanol was added. The mixture, diluted with methanol, was analyzed as before. The peaks of other compounds did not overlap with the peak of CoDMC.

Since cobalt (II) chloride was very reactive toward ZDMC in methanol, its reactivity with respect to other compounds that could have been present in extracts was investigated. It was found that neither ZnO, ZnS, nor zinc stearate reacted with cobalt (II) chloride in methanol at room temperature. The UV

spectrum of CoDMC showed an absorption maximum at 319.6 nm ($\epsilon_{319.6} = 26,244$ L/mol cm⁻¹) in methanol, but the UV spectrum of TMTD revealed its absorption to be low ($\epsilon_{319.6} = 1132$ L/mol cm⁻¹). Cobalt (II) chloride solutions did not absorb at this wavelength. A test solution containing TMTD (4 ppm) and cobalt (II) chloride (4.7 ppm) in methanol was prepared, whereupon the absorption readings at 319.6 nm were monitored as a function of time. The readings were equal to that of pure TMTD analyzed under the same conditions and remained constant over 12 h. It was concluded that TMTD and cobalt (II) chloride were unreactive under these conditions.

However, although TMTD (and TMTM) did not react with cobalt (II) chloride per se, these compounds did interfere with the zinc-cobalt exchange reaction. The following experiment was conducted in an attempt to correct for these errors. A test solution was prepared by pipetting 2.0 mL of 100 ppm TMTD and TMTM, and 10.0 mL of 100 ppm ZDMC in methanol into a 50.0-mL volumetric flask. The mixture was shaken and 4.5 mL of 250 ppm cobalt (II) chloride in methanol was pipetted into the solution. The mixture was filled to the calibration mark and contained 4 ppm TMTD, 4 ppm TMTM, and 20 ppm zinc ions in theory. Likewise, solutions containing 10 ppm TMTD, 10 ppm TMTM, and 20 ppm zinc ions and 20 ppm TMTD, 20 ppm TMTM, and 20 ppm zinc ions, and 0 ppm TMTD, 0 ppm TMTM, and 20 ppm zinc ions were made up. The latter solution served as a reference. These mixtures were analyzed with the HPLC as before, and it was evident that the absorption peak of CoDMC increased with higher concentrations of TMTD and TMTM. Since it was possible to determine the concentrations of TMTD and TMTM accurately in the vulcanizate extracts, a correction of the concentrations of ZDMC could be made.

3. Elemental Sulfur. From a stock solution containing sulfur (100 ppm), standard solutions of 40, 20, and 10 ppm were prepared. Aliquots of 20 μ L were analyzed at a flow rate of 1.0 mL/min, using a methanol-H₂O (17/3, v/v) mixture as elutriant. Sulfur ($t_R = 6.00$ min) eluted as a sharp peak, and the calibration curve was linear. The UV spectrum of sulfur revealed the ϵ_{280} value to be 5935 L/mol cm⁻¹.

A 5.0-mL aliquot of the sample master solution was diluted to 10.0 mL and analyzed as before. The compounds TMTU, TMTM, TMTD, ZDMC, and PAN did not interfere with the analysis.

The relative standard deviations calculated for duplicate HPLC experiments varied between that for TMTU (2.6%) and sulfur (0.6%).

DISCUSSION

On analyzing compounds cured in the DSC, satisfactory crosslink density values were obtained on applying the Flory–Rehner¹³ equation. The percentage of polysulfidic crosslinks was readily determined with the propane-2-thiol–piperidine¹⁴ reagent.

The initial mass of each of the vulcanizates studied was ~ 17 mg, which required the use of an ultrasensitive technique to determine the amounts of curatives, intermediates, and reaction products. The present study showed the viability of HPLC for the quantitative determination of the type and quantity of extractable products normally encountered in TMTD- or ZDMC-related sulfur vulcanization systems. These analysis proved to be essential in unravelling the mechanistic aspects of the latter vulcanization systems, as will be shown in subsequent papers in this series.

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REFERENCES

1. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2643 (1991).
2. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2661 (1991).
3. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2669 (1991).
4. D. Craig, W. L. Davidson, and A. E. Juve, *J. Polym. Sci.*, **6**, 177 (1951).
5. D. Craig, A. E. Juve, and W. L. Davidson, *J. Polym. Sci.*, **6**, 7 (1951).
6. C. G. Moore and A. A. Watson, *J. Appl. Polym. Sci.*, **8**, 581 (1964).
7. W. Scheele and C. Gensch, *Rubber Chem. Technol.*, **29**, 1373 (1956).
8. M. Kaniwa, *J. Chromatog.*, **405**, 263 (1987).
9. S. R. Hutchins, P. R. Haddad, and S. Dilli, *J. Chromatogr.*, **252**, 185 (1982).
10. ASTM D 297-81, *Annu. Book ASTM Stand.*, **09.02**, 12 (1983).
11. W. Puacz, *Acta Chim. Hung.*, **124**, 293 (1987).
12. R. J. King and D. M. Mondimore, *Rubber Chem. Technol.*, **60**, 716 (1987).
13. P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
14. B. Saville and A. A. Watson, *Rubber Chem. Technol.*, **40**, 100 (1967).

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