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Note

Analysis of Novor[®] compounds in cross-linked natural rubber products

R. P. BURFORD, J. K. HAKEN* and J. A. OBITA

Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

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Practical rubber compounds generally consists of a mixture of many components that can be conveniently categorized as polymers, fillers, plasticizers, stabilizers and curatives. Examples of formulations for most commercially important polymers are provided in standard texts¹⁻⁴. For natural rubber (*i.e.*, *cis*-polyisoprene) compounds, common reinforcing fillers such as carbon black and silica are added at levels of up to 50 parts per hundred rubber (pph), and the plasticizer is typically an aromatic oil present at levels from 5 to 15 pph.

In contrast to the polymer, filler and plasticizers, the other components are generally present in low concentrations (up to 2 pph). Traditionally, sulphur is used to cross-link natural rubber, but as the reaction is too slow for efficient commercial application, one or more accelerators are included to enable cure times to be reduced to less than 30 min. The mechanisms of sulphur cross-linking and the action of 2,2'-dithiobisbenzothiazole (MBTS), a typical accelerator, are shown in Figs. 1 and 2 (from ref. 5).

Although it is evident that sulphenamide is released during vulcanization, quantitative detection of accelerators in cross-linked rubber compounds is far from simple, as reflected by the tedious and arduous analytical scheme proposed in the *Annual Book of ASTM Standards*⁶.

If conventionally cured natural rubber compounds are subjected to further heating, a reduction in stiffness is noted. This reversion process is a significant problem, particularly when large items are to be vulcanized, as degeneration will be occurring at the surface (which has reached the cure temperature rapidly) just as the interior is attaining optimum cure. A new class of urethane cross-linking agents has been developed for reversion-sensitive natural rubber, under the generic trade-name Novor^{7,8}, to allow both reversion resistance (and hence much greater processing flexibility) and also improvement of ageing characteristics.

The mechanism for cross-linking natural rubber with urethane cross-linking agents is shown in Fig. 3⁹. Intermediatory nitrosophenols (of high toxicity)¹⁰ are formed which bind to the natural rubber. The urethane cross-link then occurs by recombination of the other intermediate, a diisocyanate. Better scorch characteristics are claimed to arise when a phenol blocked mono-adduct, as shown in Fig. 4, is used¹¹.

Novor cross-linkers can be used alone or in combination with sulphur. In the

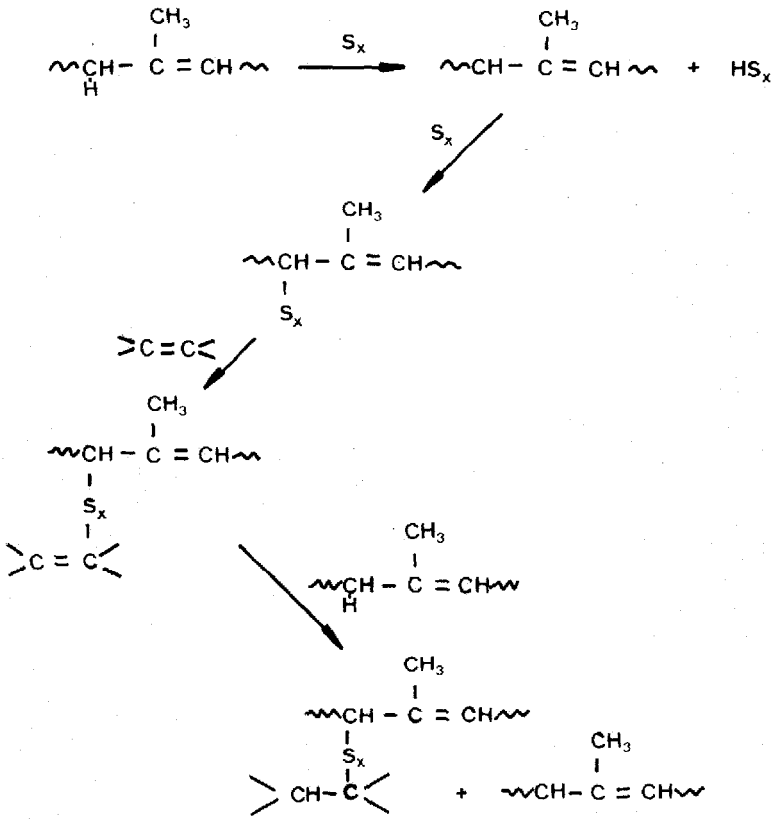


Fig. 1. Mechanism of sulphur cross-linking of natural rubber.

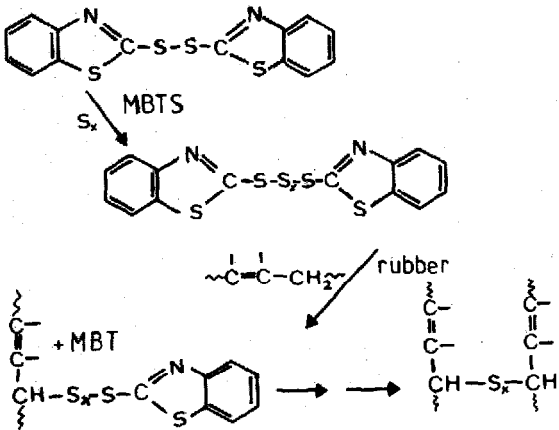


Fig. 2. Mechanism of cross-linking in the presence of 2,2'-dithiobisbenzothiazole (MBTS).

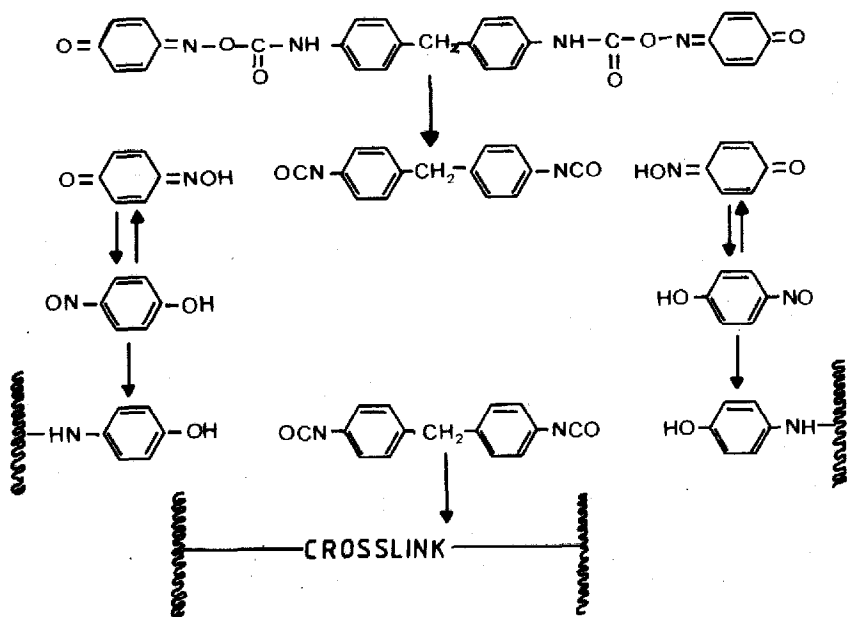


Fig. 3. Mechanism of cross-linking with urethane cross-linking agents.

latter instance only, zinc oxide and stearic acid are required. The efficiency of reaction between nitrosophenol and natural rubber is improved by the addition of zinc dimethyldithiocarbamate (ZDMC).

The examination of urethane polymers using most instrumental techniques has been reported and several reviews have appeared¹²⁻¹⁵. It is evident that the complex chemical nature is such that degradation is necessary to allow identification of the various constituents present via fragments indicative of the individual reactants.

Prolonged hydrolysis has been reported with the use of a Parr bomb apparatus and reaction with 2% sodium hydroxide solution at 150-200°C for 6-16 h¹⁶⁻²⁰ to achieve complete hydrolysis. The resulting diamines, diacids and glycols or polyols from polyester and polyether-polyurethane adducts have been identified by thin-layer chromatography, IR and nuclear magnetic resonance (NMR) spectroscopy, gas chromatography (GC) and potentiometric titration. The early methods have been refined and extended by the formation of derivatives that have allowed examination by gas and liquid chromatography.

Polyesters and polyether-polyurethanes have been fragmented by aminolysis with morpholine¹⁵, followed by analysis of the products using IR spectroscopy and GC. Hydrazine has also been used but a prior extended acid hydrolysis detracts from the value of the method¹⁵.

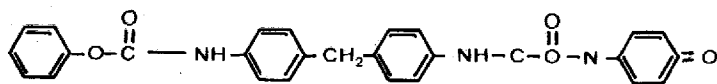


Fig. 4. Phenol blocked mono-urethane adduct.

TABLE I
FORMULATION OF RUBBER COMPOUND

<i>Component</i>	<i>Weight (g)</i>
Natural rubber (SMP Heveacrub SP20)	40
Highly abrasive furnace black	20
Highly aromatic extender oil	1.6
Zinc oxide (NBS Reference Material)	2.0
Stearic acid (NBS Reference Material)	0.4
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylene-diamine (Santoflex 13)	0.8
Novor 924	2.68
ZDMC (Methasan)	0.8

The hydrolysis reaction has been greatly facilitated by the use of alkali fusion GC, which has been applied to polyurethane materials by Gibian and Siggia¹⁹ and Birbira and Haken²⁰.

In this work we applied the above procedures to the analysis of complex urethane cross-linking agents in vulcanized natural rubber compounds.

EXPERIMENTAL

Sample preparation

A natural rubber compound was prepared in broad accordance with ASTM D3182, but using an internal mixer fitted with a Haake Rheomix type 600 mixing head equipped with cam rotors. The recipe used is shown in Table I. Two parts of zinc dithiocarbamate (ZDMC) per hundred of polymer were added to improve the cure efficiency of the Novor 924 compound.

Natural rubber was premasticated at 70°C for 1 min using a rotor speed of 60 rpm. Black, oil, zinc oxide and stearic acid were then added. After 2 min the remaining powders were provided, and the irregular-shaped mass was removed after a total mix time of 5 min. It was evident from subsequent milling and cure rheological behaviour (as measured using a Monsanto MPV cure rheometer) that the compound was about to cross-link (*i.e.*, "Scorch"). Samples of both the uncured mixture and the vulcanized tensile tension pads (prepared also according to ASTM D3182) were submitted for analysis by fusion-GC.

Fusion

The vulcanized rubber from each formulation was subjected to alkali fusion by placing small pieces in a 25-ml round bottomed flask containing the appropriate amount of the fusion-flux agent. The reaction mixture consisted of 2 g of rubber and 10 g of potassium hydroxide-sodium acetate mixture^{19,20}.

A water condenser was attached to the flask, which was then heated electrically. The mixture was refluxed for 1 h and, after cooling, sufficient water was added to dissolve the reaction products. The aqueous solution was then extracted several times with fresh diethyl ether. When no longer coloured, the ethereal layer was dried using anhydrous sodium sulphate, filtered and the volume reduced to about 50 ml.

Trifluoroacetic anhydride (TFAA) was then added to react with any extracted amine to form the TFA derivative.

The excess of TFAA was destroyed using distilled water. The liquid was cooled in ice and the crystals that separated out were recovered by filtration, dried and analysed using liquid and gas chromatography.

Liquid chromatography

The TFA derivative was dissolved in analytical-reagent grade methanol and separated on a Waters C₁₈ column using methanol-water (70:30) as the mobile phase. The chromatographic equipment consisted of a Waters Model 6000A delivery system operated at 1.5 ml/min, a Waters 710B WISP automatic sample injection system and a Waters R401 differential refractometer detector. The system was connected to a Waters 730 Data Module, which performed both electronic plotting and reporting.

Gas chromatography

An FEM 810/29 gas chromatograph fitted with flame-ionization detectors was used. An aluminium column (2 m × 3 mm I.D.) packed with Tenax GC (60–80 mesh) was used to separate the TFA derivatives. The injection port was maintained at 200°C and the column temperature was programmed from 150 to 250°C at 10°C/min. Alternatively, an FFAP column (6 ft. × 1/8 in. I.D.) operated isothermally at 250°C may be used for the separations. A flow-rate of 35 ml/min of the carrier gas (nitrogen) was found to be suitable.

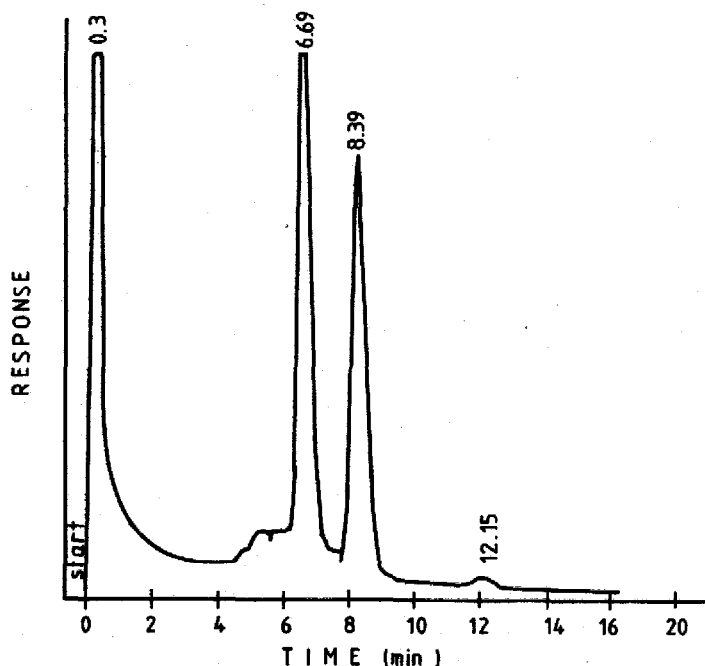


Fig. 5. Gas chromatogram showing major components resulting from degradation of natural rubber compound.

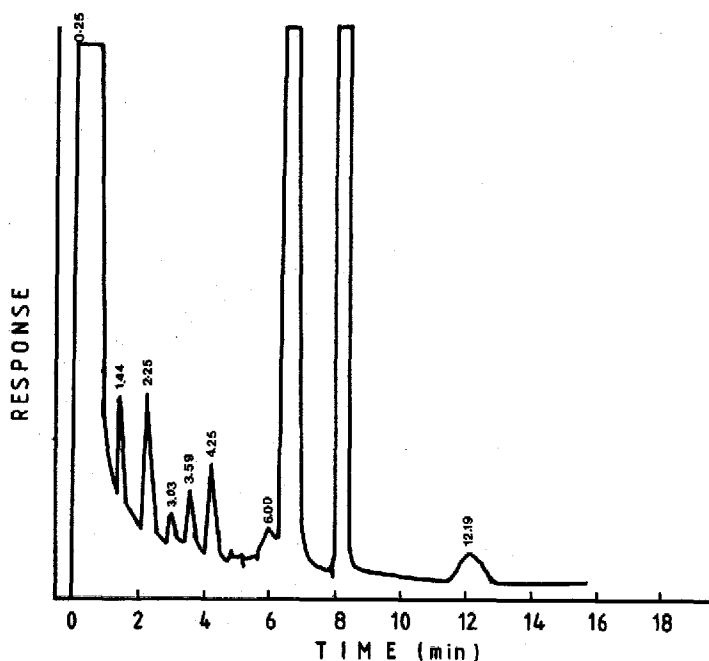


Fig. 6. Gas chromatogram showing minor components resulting from degradation of natural rubber compound.

RESULTS AND DISCUSSION

The fusion reaction successfully hydrolyses the polyurethane linkages with liberation of the corresponding diamines. The procedure used is a macro-version of that previously reported for various amide-imide polymers²¹. Examination of the Novor compound by GC after alkali fusion as TFA derivatives shows two major peaks (Fig. 5). Liquid chromatography gave similar results to GC. The first major peak (retention time 6.69 min) was identified as an aromatic diamine using mass spectrometry and was consistent with the diamine corresponding to 2,4-tolylene diisocyanate, the central fragment of the Novor 924 compounds. The second peak has the same retention as *m*-phenylenediamine (retention time 8.36 min), with the identity being confirmed using mass spectrometry. This component was not expected from a study of the relevant patent⁷; however, it is apparently present at the bismaleimide. Its identification is of some interest as the presence of *m*-phenylenediamine may also arise as a component of common staining antioxidants in rubber compounds. Compounds containing conjugated diene functionality have been reported as cross-linking agents via a Diels-Alder reaction. The dienophiles described include maleimides, which are extremely active²².

It is also possible that other components are present in the Novor, as shown by the various peaks in the chromatogram (Fig. 6). The composition of these compounds will be established by mass spectrometry as it is of interest to determine the origin of these other materials.

The fusion procedure has little effect chemically on the base rubber polymer

which, however, is submitted to vigorous mechanical and thermal action such that minor components that are not chemically bound may be readily extracted from the analysis residue and examined as appropriate. Preliminary work^{2,3} has shown that amines, phenols and ester materials are readily cleaved and the procedure as reported is being studied further as a possible general method for the analysis of additives of several functional classes that are used in cross-linked rubber products^{2,3}.

A new Novor material, a Novor 950, has recently been introduced²⁴ that incorporates an aliphatic diisocyanate, which it is expected could be determined using the procedure reported here.

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