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### Characterization of the Chemical Structure of Sulphur Vulcanizates of Natural Rubber Using $^1\text{H}$ NMR Spectroscopy

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## CHARACTERIZATION OF THE CHEMICAL STRUCTURE OF SULPHUR VULCANIZATES OF NATURAL RUBBER USING $^1\text{H}$ NMR SPECTROSCOPY

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**Abstract** Vulcanizates containing only di- and poly-sulphidic crosslinks can be transformed into soluble rubber by treatment with hexane-1-thiol/piperidine, enabling examination of the crosslink sites by  $^1\text{H}$  NMR spectroscopy in solution.

Crosslinking of natural rubber is normally achieved by sulphur vulcanization at 140-180°C, in which chains of sulphur atoms connect the allylic carbons.<sup>1</sup> The crosslinks are initially polysulphidic, but at normal cure temperatures further reactions occur, notably crosslink shortening leading eventually to monosulphides. Crosslinking renders the rubber insoluble. Thus, structural characterization of vulcanizates has been mainly limited to physical measurements to determine the concentration of crosslinks and their distribution between mono-, di- and poly-sulphides,<sup>2</sup> while the more detailed chemistry has traditionally been elucidated through investigation of the reactions of suitable model alkenes of low molecular weight.<sup>1</sup> Recently, solid-state  $^{13}\text{C}$  NMR spectroscopy has been employed to study vulcanizates,<sup>3</sup> but interpreting the spectra is problematical. Di- and poly-sulphidic crosslinks can be cleaved by treatment with hexane-1-thiol/piperidine,<sup>2</sup> leaving a thiol on each polyisoprene at the site of crosslinking. We have used this method to regenerate soluble rubber from vulcanizates and obtain  $^1\text{H}$  NMR spectra.

The formulations and cure conditions used are given in Table 1. Low cure temperatures and relatively short cure times were employed to avoid the formation of monosulphides. All of the vulcanizates dissolved in hexane-1-thiol/piperidine, confirming the absence of monosulphides. After purification  $^1\text{H}$  NMR spectra were obtained (6000-9000 transients at 400MHz in  $\text{CDCl}_3$ ). The crosslink residues were identified by correlation of chemical shift, splitting pattern and coupling constants of the  $\alpha$ -protons with those of model thiols with very similar structures (Fig. 1). Yields of crosslinks agree surprisingly well with values obtained from

physical measurements (Table 1). Also revealed in the spectra are aldehydes and epoxides arising from oxidation during vulcanization. *Z-E* Isomerization of isolated double bonds is almost negligible, suggesting that the crosslinking is not occurring by a free-radical mechanism.

TABLE 1 Formulations (relative weights; all have natural rubber, 100, zinc oxide, 5, and sulphur, 10), Cure conditions and Crosslink yields.

Vulcanizate	A	B	C	D	E		
<i>N-t</i> -Butylbenzothiazole-2-sulphenamide	0.6	0	0	0	0		
Cyclohexylammonium benzothiazole-2-thiolate	0	2.7	2.7	2.7	2.7		
Stearic acid	1	0	0	0	0		
Zinc stearate	0	0	0	0	12.6		
2,6-Di- <i>t</i> -butyl-4-methylphenol	0	0	1	0	0		
2,2'-Methylene-bis-(4-methyl-6- <i>t</i> -butylphenol)	0	0	0	2	2		
Cure temperature (°C)	100	80	80	80	80		
Cure time (h)	5	8	8	8	8		
Crosslinks (mol%)	{	by physical measurements	1.03	2.38	2.28	2.26	2.58
		by NMR	1.03	2.34	2.74	2.43	3.04

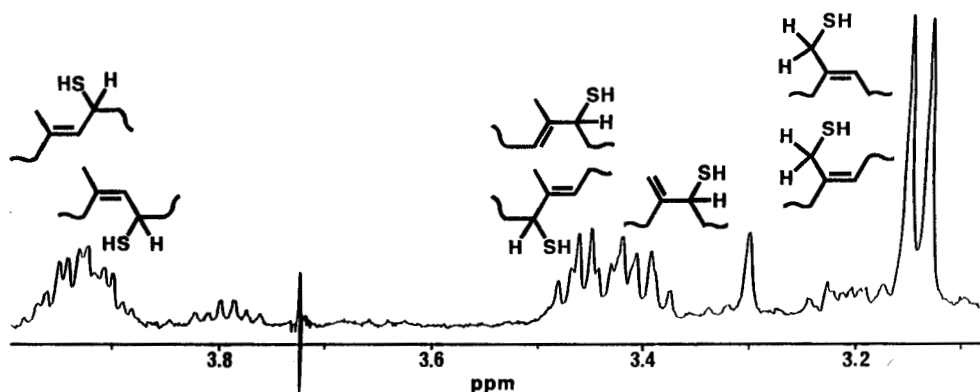


FIGURE 1  $^1\text{H}$  NMR spectrum of soluble rubber from vulcanizate C.

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