A Study of Sulfur Bridges in Filled Natural Rubber Vulcanizates by Pyrolysis Gas Chromatography with Flame-Photometric Detection

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Synopsis

Natural rubber vulcanizates of two formulations, with sulfur/N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and tetramethylthiuram disulfide (TMTD), respectively, were analyzed by pyrolysis gas chromatography. A sulfur-selective flame-photometric detector was utilized. The main pyrolysis products were identified as CS_2 and some thiophenes. The yields of the pyrolysis products from the two types of rubber were very different. The yields also varied with the curing time of the rubbers.

INTRODUCTION

The thermal and mechanical properties of vulcanized rubber are strongly affected by the different types of crosslinks.[1-4] Direct methods for estimation of the structural properties of vulcanizates include measurements of physical properties[5] such as swelling,[6] creep,[7] and stress–strain.[8,9] Specific degradation with chemical reagents, so-called chemical probes, are used in combination with stress–strain measurements[5,10,11] for relative determination of the different types of crosslinks. Despite the existing methods, there is still a demand for improved procedures to determine the types and distribution of sulfidic bridges, especially in filled vulcanizates.[5,10]

The pyrolysis technique is an established method for polymer analysis.[12] A survey of the technique applied to analysis of insoluble samples, mainly vulcanized rubber, has been made.[13] It has been shown that pyrolysis gas chromatography (PyGC) can be used with good reproducibility for the analysis of large samples.[13,14]

It was shown[13] that the sulfur content affected the yield of butadiene when vulcanized styrene–butadiene rubber was pyrolyzed. Häusler and Hube[15] found a correlation between the degree of swelling and the peak ratio of toluene/4-vinylcyclohexene from PyGC measurements of vulcanized polybutadiene. Recently, Czybulka et al.[16] studied vulcanizates by pyrolysis field ionization mass spectrometry with special attention to the components present in low concentration, viz., comonomers, accelerators, metal oxides, and antioxidants.

In the PyGC studies mentioned,[13,15] a flame ionization detector was used. The sulfur-containing pyrolysis products should be of special interest for the study of sulfur bridges. Sulfur-containing products can be selectively detected with a flame-photometric detector.[17] A flame-photometric detector has earlier been used together with PyGC for quantitative determination of aliphatic sulfur-

containing additives.[18]   The additives were extracted from the polymer prior to pyrolysis.

As a first step in the elucidation of the sulfur bridges in filled vulcanized rubbers by PyGC, the sulfur-containing pyrolysis products were studied in the present work.

EXPERIMENTAL

Apparatus and Operating Conditions

The pyrolyzer consists of a thin (0.012 mm) platinum foil 15 mm long and 2.6 mm wide.   The edges of the foil were bent upward at the middle in order to prevent the sample from falling off the foil.   The foil was heated by two current pulses.   The first, 8 ms long, increased the temperature of the pyrolyzer to the desired pyrolysis temperatures.   The second, the length of which could be varied, compensated for heat losses so that the temperature of the pyrolyzer was constant.   The pyrolyzer was connected directly to the column of the gas chromatograph.   After each pyrolysis, the glass walls of the pyrolysis chamber were cleaned with acetone.

The operating conditions were as follows: pyrolyzer, foil pulse[19]; pyrolysis chamber temperature, 70, 115, and 175°C; pyrolysis temperature, 600, 800, 1000, and 1200°C; pyrolysis time, 0.2 and 0.5 s; gas chromatograph: Varian 1860; column, 3.5 m × $\frac{1}{8}$ in., 1.9 mm i.d., stainless steel; column packing, 10% Carbowax 20 M on Chromosorb W, AW, 80/100 mesh; column temperature, programmed 50–250°C, 20°C/min; flow rates, N_2 20.0 mL/min, H_2 80 mL/min, air 80 mL/min; detector, flame photometric, Micro Tek Instrument Corporation, Austin, TX; detector temperature, 125°C; integrator, CDS 101; mass spectrometer, Finnigan 4021.   The integrals of the registered peaks measured by the integrator are given in integrator counts (i.c.).

Samples and Preparations

The formulations of the samples investigated are listed in Table I.   The samples named A_R and B_R were used as references as they had been analyzed for the crosslinks by RAPRA,[20] Table II.   These samples had been vulcanized for 33, 50, and 66 min at 140°C.   The A_R and B_R vulcanizates were treated with

TABLE I
Formulations of Rubber Materials (Weight Parts per 100 Parts NR)

	Samples A_R, A	Samples B_R, B
Natural rubber, NR	100	100
Carbon black, SRF	50	50
ZnO	5	5
Stearic acid	1	1
CBS[a]	0.6	—
Sulfur	2.85	—
TMTD[b]	—	4

[a] N-Cyclohexyl-2-benzothiazolesulfenamide.

[b] Tetramethylthiuram disulfide.

TABLE II
Network Analysis made by RAPRA[a]

	Sample A_R			Sample B_R		
	33 min[b]	50 min	66 min	33 min	50 min	66 min
% Polysulfide crosslinks	75	76	51	17	9	5
% Disulfide crosslinks	25	24	49	29	31	22
% Monosulfide crosslinks	—	—	—	54	60	73
$S_{total}\%$ (extracted)	1.96	2.12	2.22	0.82	0.74	0.80
$S_{sulfide}\%$	0.20	0.24	0.28	0.02	0.02	0.05
$S_c\%$	1.76	1.88	1.94	0.80	0.72	0.75
ϵ	9.4	9.2	11.6	5.7	4.5	5.1

[a] $S_{total}\%$: Total sulfur content, (w/w); $S_{sulfide}\%$: inorganic sulfur, % (w/w); $S_c\%$: sulfur combined in the network; ϵ: the Moore efficiency parameter defined by S_c/crosslink density.

[b] Vulcanization time.

propane-2-thiol and piperidine in n-heptane to cleave the polysulfidic crosslinks and in n-hexanethiol and piperidine to break the polysulfidic and disulfidic crosslinks.

The samples named A and B had been vulcanized at 140°C for 10, 30, 50, and 70 min. They were used to study the influence of the curing time over a longer period. Furthermore, as the formulations were the same as for the A_R and B_R systems, they were used to check the reproducibility of the vulcanization.

The samples were Soxhlet extracted for 24 h with an azeotropic mixture of acetone, chloroform, and methanol (3.5:2.9:2.7 by volume) to remove any residues of sulfurous compounds not combined in the polymer network. The samples were cut into small, thin pieces and weighed on a Sartorius microbalance. The samples weighed 30–50 μg.

The total sulfur content of the samples was determined by elemental analysis.[21]

The reference compounds for the identification of pyrolysis products were either commercial products or synthetic preparations. Gaseous reference materials were hydrogen sulfide and carbonyl sulfide (The Matheson Co., Atlanta, GA) and sulfur dioxide (Alfax AB, Malmö, Sweden). Other compounds were carbon disulfide (p.a., E. Merck AG, Darmstadt, W. Germany); thiophene (Vondelingenplaat, Rotterdam, Holland); methane-, ethane-, and n-pentane-thiols (Eastman Organic Chemicals, Rochester, NY): n-propane-, n-butane-, and n-hexanethiols and 2-propene-1-thiol (Fluka AG, Buchs, Switzerland); n-monosulfides, $(C_nH_{2n+1})_2S$, $n = 1$–6; n-disulfides, $(C_nH_{2n+1}S)_2$, $n = 1$–5; 2-methylthiophene; and 3-methylthiophene. The compounds were dissolved in acetone (1:10^3 by volume). The injection volume was 1 μl. Some of the solutions were also used to determine the detector response factors.

RESULTS

Test of Chromatographic and Detection Conditions

Column packings of different polarity were tested. Carbowax 20 M on an unsilanized support was found to give a good separation and symmetric peaks of the sulfurous compounds. The sensitivity of the detector increased with decreasing flow rates of hydrogen and air. At too low air flow rates ($\leq$60 mL/

min), the flame became unstable. Equal flow rates of hydrogen and air of 80 ml/min were found to give a stable signal and high response factors for sulfurous compounds.

The relation between the detector response and the concentration of sulfurous compounds was determined. Eckhardt et al.[17] showed that the order of the response of the FPD was much dependent of the gas flows. Therefore, different concentrations of carbon disulfide solutions were injected. The logarithm of the registered peak area was plotted vs. the logarithm of the amount of carbon disulfide injected. A straight line with slope 2.0 was obtained. Consequently, the square root of the peak areas should be a linear function of the amount of sulfurous substances. The sulfur-to-carbon selectivity was estimated to be 4 $\times 10^5$ from the detector response for carbon disulfide and acetone.

Table III shows the molar response factors for some products.

Identification of Pyrolysis Products

Figure 1 shows examples of pyrograms obtained from the two vulcanizing systems. No peaks could be specifically ascribed to any of the two vulcanizing systems. The identification was made from comparison with retention data for injected sulfurous compound solutions. Mass spectrometry did not provide reliable identification due to the large background signals from the hydrocarbons. Injection of hydrogen sulfide and the thiols on the Carbowax column yielded very irreproducible results, probably owing to adsorption or reactions in the chromatographic system.[22] Therefore, it was not possible to establish whether hydrogensulfide, methanethiol, and 2-propene-1-thiol were pyrolysis products from vulcanized natural rubber, which has been suggested earlier.[6]

None of the thiophenes, thiols, sulfides, and disulfides tested gave retention data corresponding to peak 6.

Natural rubber pyrolyzed together with elemental sulfur or TMTD gave much the same pyrolysis products as the A_R samples. Natural rubber and carbon black together gave negligible peaks.

Pyrolysis Chamber Temperature

Samples of the A_R and B_R vulcanizates were pyrolyzed at chamber temperatures of 70, 115, and 175°C. The pyrograms obtained at 70 and 115°C were very similar. The yields of high-boiling products did not increase at 175°C. Condensation of possible high-boiling sulfurous products was therefore negligible. At 175°C, which is much higher than the vulcanization temperature, 140°C, degradation was observed. A chamber temperature of 115°C was therefore chosen.

TABLE III
Flame-Photometric Detector Response Factors for Sulfurous Compounds

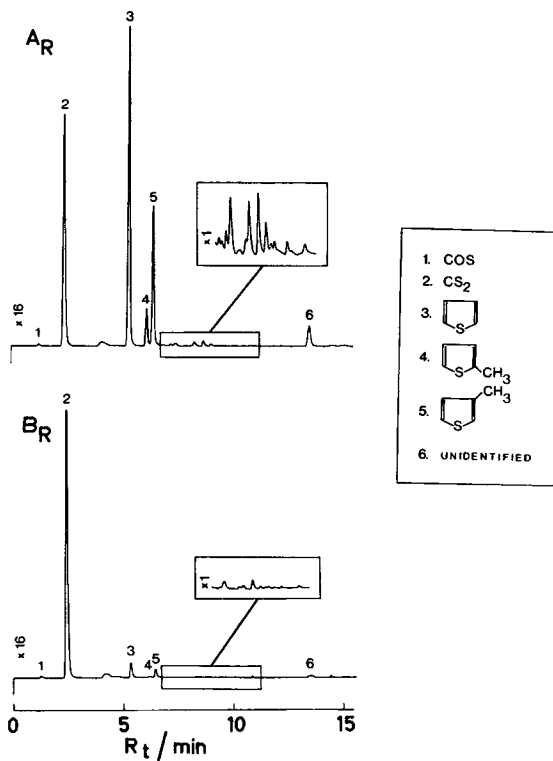| Substance	(Integrator counts)$^{1/2}$ per mole S
CS_2	3.2×10^{11}
Thiophene	6.3×10^{11}
2-Methylthiophene	8.3×10^{11}
3-Methylthiophene	8.5×10^{11}

Fig. 1. Pyrograms of 37 μg A_R33 and 33 μg B_R33 pyrolyzed at 1000°C for 0.2 s.

Pyrolysis Temperature

The samples A_R50 and B_R50 were pyrolyzed at different pyrolysis temperatures. The time was chosen long enough to yield complete pyrolysis for the sulfurous compounds, viz., 0.5 s at 600°C and 0.2 s at the higher temperatures. The yields of the main products are plotted vs. the pyrolysis temperature in Figure 2. The total sulfur content of the pyrolysis products is given in Table IV. The response factors given in Table III were utilized for the calculations. For the products not given in Table III, a value of 7.5×10^{11} (integrator counts)$^{1/2}$ per mol S was used.

Precision

The relative standard deviations for the different product yields are shown in Table V. The variation of the yields from samples extracted on different occasions was not significantly greater than those from samples from the same extraction. No significant change of the yields was observed when the foil was changed.

Pyrolysis of Different Vulcanizing Systems

Figure 3 shows that the peak pattern is completely different for samples of the A and B series. A_R and B_R are the same rubbers as A and B, as they were made with the same formulations but on different occasions. The analysis
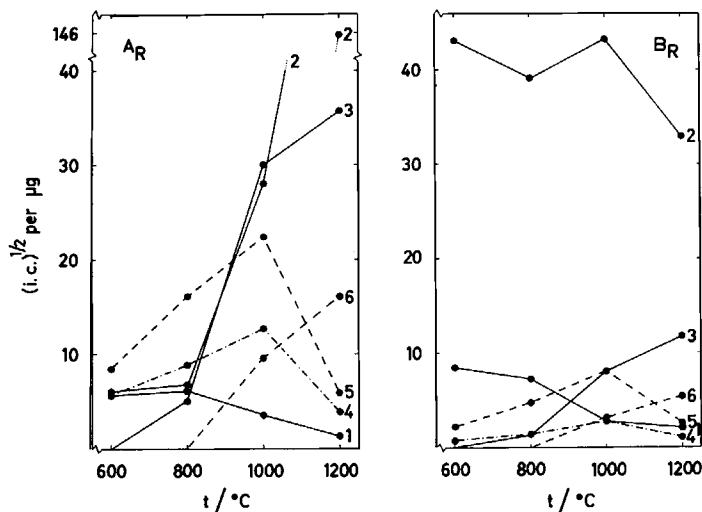
Fig. 2. Yield of the different pyrolysis products marked in Fig. 1 plotted vs. pyrolysis temperature. The samples were A_R50 and B_R50. Pyrolysis time: 0.5 s at 600°C and 0.2 s at the other temperatures.

presented in Table II shows that the polysulfide content of the A_R is dominating, whereas the B_R series is dominated by the monosulfides according to the method used. A more detailed information of the yields of pyrolysis products is provided in Table VI. Besides the production of products from the original samples (extracted), the effect of the chemical treatment of the A_R and B_R rubbers is given.

From the yields of the sulfurous pyrolysis products, the sulfur content of the samples was estimated (Table VII).

Sulfur Analyses

The results from the elemental total sulfur analyses are given in Table VIII. The table also shows the amount of sulfur calculated from the formulations, S_{calc}. The components were supposed to be pure. For most of the samples, only single

TABLE IV
Sulfur Content % (w/w) Obtained from Pyrolysis

Sample	600°C	800°C	1000°C	1200°C
A_R50	0.36	0.64	1.14	2.05
B_R50	0.53	0.62	0.65	0.52

TABLE V
Precision Obtained for the Different Pyrolysis Products of the Vulcanizate A_R33 During Three Weeks[a]

Peak	1	2	3	4	5	6
$\bar{x},/\sqrt{\text{i.c.}} \times \mu g^{-1}$	2.96	25.4	29.0	11.2	21.2	9.20
$(s/\bar{x}) \times 100$	10.7	13.0	8.8	4.4	4.3	11.5

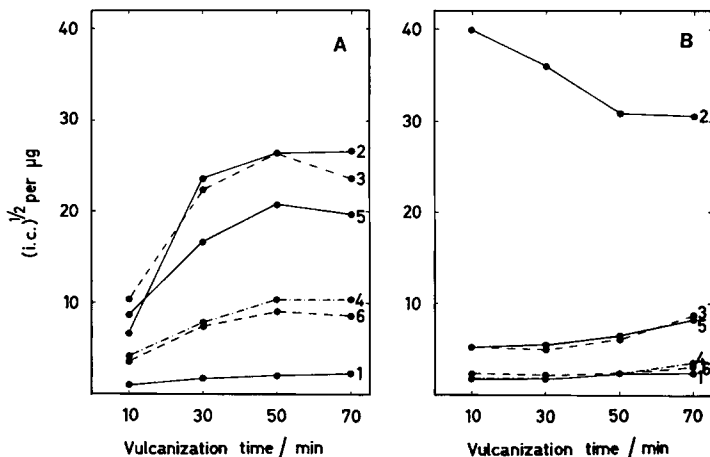[a] $n = 13$; pyrolysis at 1000°C for 0.2 s.

Fig. 3. Yield of the pyrolysis products marked in Fig. 1 plotted vs. vulcanization time. To the left, the A series; and to the right, the B series. Pyrolysis temperature and time: 1000°C and 0.2 s.

determinations were made as the imprecision of the method should be less than 2%.

DISCUSSION

Sulfur is bound into vulcanized rubber as different types of sulfidic bridges, causing crosslinks of the rubber, but also as cyclic sulfides or as pendent groups which do not take part in the crosslinking.[10] The two vulcanizing systems were chosen to represent materials with different composition of sulfur bridges.

From Figures 1, 2, and 3, it is evident that the pyrolysis pattern is quite different for the two curing systems. As all the samples were Soxhlet extracted before pyrolysis, the interferences from the unreacted curing agents could be excluded, and the sulfurous pyrolysis products detected should only originate from sulfur combined with the polymer. The fact that reactions between fragments formed during pyrolysis of the mixtures occurred implies that the sulfurous pyrolysis products formed from combined sulfur could as well be secondary reaction products as pure degradation fragments.

As no specific peaks were found for any of the samples, the pyrolysis conditions were chosen to yield results as characteristic as possible for each sample. Thus, at 1000°C the pyrograms of the samples with varying curing times showed the greatest variations.

Lower energies are needed to break the sulfidic links than to break the carbon links of the polymer chain.[2] At low pyrolysis temperatures (<400°C), where little degradation of the polymer chain is expected, very low yields of detectable sulfurous compounds were obtained. In contrast to the hydrocarbon production,[23] repeated pyrolysis at higher temperatures did not increase the yield. This indicates that nonvolatile products, including elemental sulfur, condensed on the walls of the pyrolysis chamber or at the initial part of the chromatographic column. The higher the temperature, the greater was the total yields from the A system, while for the B system the total yields were relatively constant (Table IV). At 1200°C, all the sulfur in the A samples could be accounted for as volatile products (Tables IV and VIII).

TABLE VI
Yields of Products Marked in Figure 1 for Vulcanizates Pyrolyzed at 1000°C for 0.2 s.

Peak no.	Pyrolysis product	Sample preparation[a]	Yield/$\sqrt{\text{i.c.}} \times \mu g^{-1}$					
			A_R33	A_R50	A_R66	B_R33	B_R50	B_R66
1	Carbonyl	Extracted	3.0	3.5	4.8	2.8	2.8	2.8
	sulfide	Polysulfide	· 2.8	3.4	2.7	2.5	2.5	2.4
		Disulfide	2.0	2.3	2.7	1.7	1.8	2.1
2	Carbon	Extracted	25	28	31	45	43	43
	disulfide	Polysulfide	33	37	35	34	35	35
		Disulfide	22	27	33 ·	25	25	26
3	Thiophene	Extracted	29	30	28	6.1	8.1	7.6
		Polysulfide	25	26	27	8.8	7.4	8.0
		Disulfide	20	30	32	11	14	13
4	2-Methyl	Extracted	11	13	13	2.1	2.8	2.5
	thiophene	Polysulfide	9.8	12	9.7	2.5	2.2	2.4
		Disulfide	6.6	11	12	3.1	3.7	3.6
5	3-Methyl	Extracted	21	22	22	5.7	8.0	6.9
	thiophene	Polysulfide	18	21	17	6.8	6.8	6.9
		Disulfide	12	20	21	8.5	9.5	10
6		Extracted	9.1	9.6	9.0	2.4	3.1	2.9
		Polysulfide	8.3	8.6	8.8	3.2	2.8	3.0
		Disulfide	6.2	8.8	9.7	3.3	3.9	3.6
			A10	A30	A50	A70	B10	B30	B50	B70
1		Extracted	1.1	1.8	2.1	2.3	1.7	1.8	2.4	2.4
2		Extracted	6.7	24	26	27	40	36	31	31
3		Extracted	10	22	26	24	5.3	5.0	6.1	8.8
4		Extracted	4.2	7.9	10	10	1.9	1.8	2.4	3.5
5		Extracted	8.7	17	21	20	5.2	5.5	6.5	8.2
6		Extracted	3.6	7.5	9.1	8.6	2.4	2.2	2.4	3.1

[a] Samples marked "extracted" had just been extracted with the azeotropic solvent mixture, "polysulfide" were treated to break polysulfidic links before extraction, "disulfide" were treated to break both poly- and disulfidic links before extraction.

The production of carbon disulfide seems to include several reactions. One contribution to the sudden increase of the yield at 800°C for the A system could be sulfur from the polysulfide links starting to react with carbonaceous fragments. For the B system, carbon disulfide was formed in high amounts even at low temperatures. Moreover, there was no increase at the highest temperatures. This indicates that for the B system, another reaction is involved in the carbon disulfide production. Possibly pendent sulfurous groups[10] from reacted TMTD contribute to the production of carbon disulfide. The A system (see Fig. 2) gave only very little carbon disulfide at 600°C in comparison with the B system. The

TABLE VII
Sulfur Content % (w/w) Obtained from Pyrolysis (1000°C, 0.2 s) of Samples Treated as Described in Table VI

Sample preparation	A_R33	A_R50	A_R66	B_R33	B_R50	B_R66
Extracted	0.89	1.14	1.16	0.60	0.65	0.67
Polysulfide	0.95	1.04	0.92	0.50	0.49	0.53
Disulfide	0.61	0.80	1.01	0.47	0.50	0.51

TABLE VIII
Sulfur Content % (w/w)[a]

Vulcanization system	A_R33	A_R50	A_R66	B_R33	B_R50	B_R66	SRF	NR + SRF 2:1 w/w
Untreated samples								
S_{calc}	1.88	1.88	1.88	1.33	1.33	1.33	0	0
S_{exp}	1.97	2.20	2.32	1.57	1.71	1.61	0.46	0.34
Extracted samples	1.87	2.08	2.21	0.94	0.88	1.04		
After polysulfide cleavage	1.85	2.00	2.28	0.81	0.79	0.76		
After disulfide cleavage	1.20	1.67	1.85	0.81	0.83	0.85		
	A10	A30	A50	A70	B10	B30	B50	B70
Untreated samples								
S_{calc}	1.88	1.88	1.88	1.88	1.33	1.33	1.33	1.33
S_{exp}	2.00	1.96	2.11	2.07	1.38	1.36	1.39	1.36
Extracted samples	0.85	1.84	1.85	2.00	0.42	0.50	0.49	0.47

[a] S_{calc}: Calculated from the sulfurous compounds of the formulations, S_{exp}: found by elemental sulfur analysis.

production of carbon disulfide at 600°C could reflect the amount of disulfide bridges of the samples.

The production of thiophenes and peak 6 varied with the temperature in essentially the same way for the two systems but with different yields. The A_R system produced about four times more thiophenes than the B_R system. Cyclic monosulfides which are assumed to be present in vulcanized rubber[2,10] could be the origin of the production of the thiophenes. Sulfur atoms from the polysulfide chains, reacted with hydrocarbon fragments, could also be the source for thiophene formation.

The production of carbonyl sulfide varied in much the same way for the two systems with the pyrolysis temperature. Most probably it originates from reactions with the oxygen-containing zinc oxide and/or stearic acid.

After the cleavage of the polysulfide bridges, the amount of CS_2 increased about 30% for the A_R system. The reason might be that the propane-2-thiol combines with the sulfur left on the polymer chain to form disulfide bridges.[11] The total amount of sulfur did not change (Table VIII). If the average length of the polysulfide bridges is S_4 and two atoms from the thiol are added to the chains while the two central atoms of the bridge leave, the sulfur content should be constant. The amount of thiophenes decreased correspondingly, which indicates that sulfur from the polysulfide bridges no longer was available for thiophene formation.

The propane-2-thiol treatment affects the B system in a different way than the A system. Both the total yield of pyrolysis products and the sulfur content of the B samples decreased. The explanation could be that there are sulfurous groups from the TMTD, not to be found in the A_R system, which are influenced by the propane-2-thiol treatment. It seems improbable that the B samples would contain any appreciable amount of polysulfide links with more than four sulfur atoms.

After breakage of the disulfide bridges of the B samples, the yield of carbon disulfide decreased compared with both the untreated and the propane-2-thiol-treated B samples (Table VI). This would further confirm that disulfide

links are a source of carbon disulfide. The results for the A samples are not directly comparable, as the pyrolyses were made at 1000°C where other types of reactions seem to dominate. The yield of thiophenes increased noticeably for the B system. Therefore, it is tempting to assume that cyclic monosulfides are formed from disulfide bridges treated with hexanethiol. The yield of thiophenes from the A samples was less altered, which is in consequence with the proposed mechanism of thiophenes also being formed from polysulfide sulfur atoms.

The vulcanization of S/CBS systems is known to be slower than that of TMTD systems.[24] Though the origin of the products is not known yet, the progress of the vulcanization is reflected in the product yields (Fig. 3 and Table VI). The slopes of the curves (Fig. 3) show a slower vulcanizing process for the A sample than for the B sample. This is further indicated by the sulfur content of the extracted samples of the A and B series (Table VII).

Several parameters could influence the precision of the product yields. Adsorption of sulfurous products (predominantly thiols) on the inner wall of the column and on the surface of the support could not be excluded.[22,25] It was found that the sample size had to be kept within a small interval (40 ± 10 μg) for an acceptable precision. This indicates that the thermal degradation reaction and other reactions are sensitive to the temperature gradient in the sample. An insoluble sample cannot be placed on the bent foil as reproducible as a sample solution can be applied to a flat foil. Inhomogeneities of the samples and catalysis from the Pt foil could also increase the standard deviation.

The reproducibility of the batches is given by Tables VI and VIII. Lower yields of pyrolysis products and lower total sulfur contents were obtained for the extracted A and B samples than for the extracted A_R and B_R samples. The yield of the pyrolysis products was proportional to the sulfur content of the A_R and A samples. Therefore, the variation could be simply explained by different sulfur content of the initial unvulcanized mixtures. The differences between the yields of the pyrolysis products from the B_R and B samples were smaller than the differences of the total sulfur content of these samples. In addition, the progress of the vulcanization differed between the B_R and the B samples. Thus, the efficiency of the curing agents seems to vary.

The absolute values of the number of crosslinks reported by RAPRA were certainly approximate. They were based on estimation of quantities which could only be measured with the unfilled material. Thus, merely the relative values could be reliable. Furthermore, only the sulfidic crosslinks were taken into account. Carbon–carbon crosslinks could as well be present. Therefore, it was not meaningful to make a closer quantitative comparison between the results from the RAPRA analysis and from the pyrolysis.

CONCLUSIONS

This study has shown that PyGC with a sulfur-selective detector could provide valuable information about various types of vulcanizing systems, the progress in the vulcanization, and batch reproducibility. A much more detailed study, including measurements on well-defined model compounds, is necessary before any definite qualitative and quantitative determinations could be made. The diagnostic power of the method should increase with selection of a lower pyrolysis temperature and a chromatographic system more suitable for hydrogen sulfide and thiols.

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