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Elastomers: Sulphur or Peroxide Cross-linked?

An Analytical Approach

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SUMMARY: The analytical methods presented in this study lead to a characterisation of the vulcanisation system of unknown elastomers. The **chemical determination** of sulphur gives a first impression of the system. However, it cannot be proved with any degree of certainty weather a product is sulphur cross-linked or not. Other wet chemical methods (colour reactions) are more suitable for quality control of already known systems. Most **spectrometric methods** (infrared spectrometry, Raman spectrometry, nuclear resonance spectrometry) are only of use for special applications and for research. A more precise characterisation is obtained by means of **chromatographic methods,** i.e. by identifying the products, which originated from thermal degradation of the cross-linking reagents (sulphur, sulphur donators, peroxides. Evolved-Gas-Analysis (EGA) and pyrolysis gas chromatography with adequate detectors proved to be very successful as chemical-analytical methods for such investigations. In order to make a reliable statement about the vulcanisation system of unknown elastomeric material, the results of several analytical methods have to be collected and evaluated.

Introduction

This overview about analytical tools to characterise elastomeric materials and specially the cross-linking systems was worked out for users. It is based on available literature, experience and own works in our laboratories.

It was our aim to crack the cross-linking system and the agents used for cross-linking elastomeric materials with high certainty. Analytical tools and their usefulness are discussed and an approach to answer the title question is presented.

Cross-linking Mechanisms

The reaction between the mainly amorphous polymer chains and vulcanisation agents during the vulcanisation process of a compounded rubber leads to an irreversible wide-meshed three-dimensional cross-linked system. This net is responsible for the elasticity of the rubber. Cross-

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linking systems of actual economic interest based on sulphur, sulphur-donors or peroxides will be shortly illustrated.

The sulphur vulcanisation of C=C double bonds containing elastomers leads to the formation of sulphur containing cross-links between the polymer chains. Systems with sulphur and accelerators or/and retarders produce rather long chained bridges with several sulphur atoms ($-S_x-$, $x \geq 2$), whereas in systems with sulphur donors (e.g. tetramethyl thiurame disulfide, TMTD) only short chains ($-S_x-$, $x = 1, 2$) or even C-C-connections can be observed. Accelerators or/and retarders are added to control the vulcanisation process. This process changes these agents feature. Fig. 1 shows typical reaction products [1].

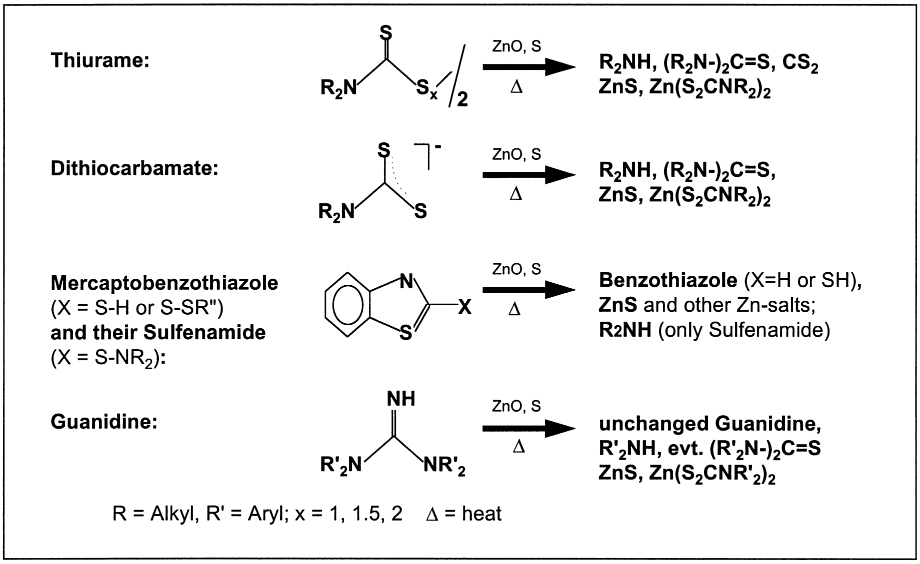

Fig. 1: Reaction products of accelerators in sulphur vulcanised rubber

Organic peroxides can be used for the vulcanisation of nearly all elastomeric materials. They decompose during the process to radicals, which react with the polymer chains and develop C-C-connections or even chain scissions. The reaction speed is controlled not by additives but by choose of the peroxide. During the vulcanisation peroxides are decomposed to alcohols, ketons and aldehydes as shown in Fig. 2 [2]. An additional tempering process often removes these mainly volatile compounds, which can influence the product properties. In ethylene-propylene-diene copolymer (EPDM) compounds sometimes some sulphur is added to remove the stickiness of the surface of the product [3].

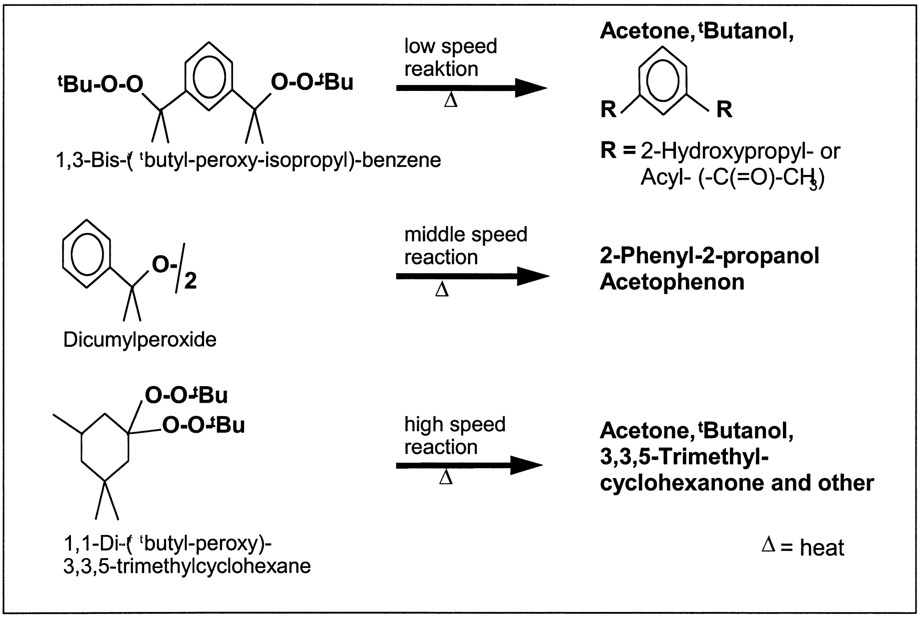

Fig. 2: Reaction products of peroxides in vulcanised rubber

Analytical Tools

This chapter describes analytical methods for the characterisation of cross-linking systems and discusses their advantages or disadvantages.

Qualitative and Quantitative Analysis

The qualitative proof of the presence of organic bound sulphur according Lassaigne is quite sensitive: 0.2% sulphur can be detected easily. The presence of sulphur in a rubber gives no certainty for sulphur containing vulcanisation system. Other organic additives as shown in Table 1 can lead to interferences!

The quantitative determination of organic bound sulphur is a central method to determine the cross-linking system. Normally soft rubber formulations contain 1-5% sulphur, those of hard rubbers (ebonite) up to 30%. Methodically the rubber is destroyed under oxidising media (i.e. according to Parr, Wurzschmitt or Schöninger) to inorganic and water soluble sulphate salts.

The sulphate content is either determined by titration (i.e. with barium chloride solution) or ion chromatography.

Using those methods, all organic sulphur containing compounds including the additives in Table 1 are recorded. Inorganic fillers (i.e. metal sulphates) do not interfere. Minor findings are observed in the presence of calcium (i.e. from chalk), lead and zinc (i.e. from zinc oxide). Treating the aqueous solution with an ion exchanger 4) can eliminate the interference of zinc. The sulphur contents in rubbers determined according the described methods differ from the calculated receipt contents; 70-95% of the calculated value are refound: During the vulcanisation process reaction products arise, which evaporate (i.e. CS_2 from TMTD) or which are not detectable (i.e. ZnS).

Table 1. Not in the vulcanisation process involved sulphur containing additives in rubbers

Type	Example
Organic plasticisers	• Alkyl-polyether-thioether
Organic stabilisers	• Distearyl-thiodipropionate
Organic modifiers	• Sulphur in peroxide cross-linked rubbers to reduce stickiness
Organic fillers	• Sulphur (≈30%) in ebonite powder
Inorganic fillers	• Baryte ($BaSO_4$)
Inorganic pigments	• CI pigment blue 29 ($Na_{6-8}Al_6Si_6O_{24}S_{2-4}$) • CI pigment orange 20 (CdS)

In order to get more information about the vulcanisation system, we highly recommend to quantify the sulphur content before and after a solvent extraction (i.e. Soxhlet extraction with chloroform or acetone). It is to consider that up to 30% of sulphur containing vulcanisation additives can be extracted! The difference between the contents before and after extraction can possibly point to other, not in the vulcanisation involved additives described in Table 1.

According our experience rubbers are probably sulphur cross-linked under the following conditions:

- In relation to the polymer content the sulphur content is before and after extraction higher than 0.7%.
- It can be shown by other analytical tools that not in the vulcanisation involved additives can be excluded.

But: The quantitative determination of the sulphur content gives no absolute certainty for the presence of a sulphur cross-linking system!

Today other wet chemical methods 5) for the detection of vulcanisation additives (by colour reactions or thin layer chromatography) or for the determination of the bridging type are slowly displaced by newer and more secure instrumental analytical methods.

Spectrometry

Infrared (IR) spectrometry 6) is qualified mainly for material characterisation. Spectra of usual rubbers do not allow any conclusions about the vulcanisation system. Only in plasticiser free materials IR spectra of solvent extracts can give sometimes evidence of used accelerators in sulphur cross-linked systems.

Raman spectrometry 7-10) has now achieved its place as an analytical tool because of the rapid development of the laser technology. But the instruments are still quite expensive. With Raman spectrometry rubbers can be qualified complementary to IR spectrometry. Compared with IR spectrometry less interferences with polar functional groups (i.e. of fillers as chalk or silicate) occur. But the intensity of the Raman emission signal can be strongly affected by NIR light absorbing materials (i.e. carbon black). Raman spectrometry sometimes points to sulphur cross-linked systems: Emission signals between 400 and 600cm^{-1} can indicate -S-S-bonds.

Also the nuclear magnetic resonance (NMR) spectrometry and especially for cross-linked materials the solid state NMR spectrometry is useful for the material identification 11-14). To characterise the polymer we recommend extracting the rubber with organic solvents. Nevertheless for good results a lot of resources have to be available:

- need of expensive spectrometric infrastructure
- difficult sample preparation (milling at -200°C)
- long measuring time (several hours) at elevated temperature (i.e. 90°C) for non intense signals

Conclusions about the cross-linking system are not easily possible 15-17). Chemical shifts of the sulphur bound carbon atoms show a certain low field shift (to 35-60ppm depending on the surroundings in the polymer chain), which can be detected in model mixtures. In real soft rubbers with 1-2% sulphur the proof of the presence of a signal or even the classification of a detected signal can be very difficult. A distinction between sulphur and peroxide cross-linking systems is therefore rarely possible.

X-ray fluorescence analysis enables a rather rapid qualitative determination of the present elements (from atomic number 11 = sodium) in materials. Sulphur can be easily detected at concentrations higher than 100ppm. We recommend measuring materials before and after solvent extraction to get a feeling about possibly interfering compounds listed in Table 1. In the extracted material mainly ebonite and inorganic fillers or pigments can interfere.

Chromatography

There exist two main ways to characterise the cross-linking system of elastomeric materials by gas chromatography (GC):

- the analysis of volatile compounds
- the analysis of pyrolysis products

The analysis of volatile compounds, which arise from the vulcanisation process and which do not evaporate, can be made by GC coupled with a mass spectrometer (MS) as detector. Two different methods can be applied:

First a solvent extract can be investigated. In this case it can happen that decomposition products can not be detected because of interfering signals deriving from plasticisers.

The second method is often a more valid tool based on evolved gas analysis (EGA): An untreated sample of rubber is placed in a suitable flask (head space flask, thermodesorption tube, alox pan for thermogravimetry), and then is heated for several minutes at 200°C. The evaporating gases are quenched in a cryo trap at -200°C. This condensate is subsequently heated up and injected in the GC.

This method allows identifying also highly volatile compounds as CS_2. Interferences of plasticisers or decomposition products of the polymer itself do rarely occur compared with the extract analysis. Even with tempered peroxide cross-linked rubbers typical decomposition products according to Fig. 2 could be detected in small amounts.

Pyrolysis coupled with GC/MS [20-23)] is another very helpful method for the identification of the polymeric structures of rubbers and the vulcanisation system. A preferably solvent extracted rubber is decomposed under inert gas (He, N_2) at 600°C, the produced volatile reaction products can be analysed directly by GC/MS. Most signals in the chromatogram derive from the polymer, but several detected compounds give direct information about the vulcanisation system. Mainly sulphur cross-linking systems produce during pyrolysis sulphur containing reaction products such as CS_2, H_2S, short chain thioethers and polymerspecific organics. Together with thiurame or dithiocarbamate accelerators more CS_2, with thiazole and sulfenamide accelerators the typical benzothiazole can be detected. If those described compounds are absent, other vulcanisation systems generally with peroxide can be expected.

The chromatograms of a pyrolysis-GC represent often a jungle of signals. It is sometimes absolutely not easy to find selective decomposition products deriving from the cross-linking system. To select sulphur-containing compounds a flamephotometric detector (FPD) 24) or an atomic emission detector (AED) 25) can be useful. Fig. 3 shows the advantageous Pyrolysis-GC/AED chromatograms of a typical EPDM formulation.

In summary it has been shown that chromatographic methods are the most promising analytical tools for both identification of the polymer, plasicisers and the characterisation of the vulcanisation system in rubber products with unknown compositions.

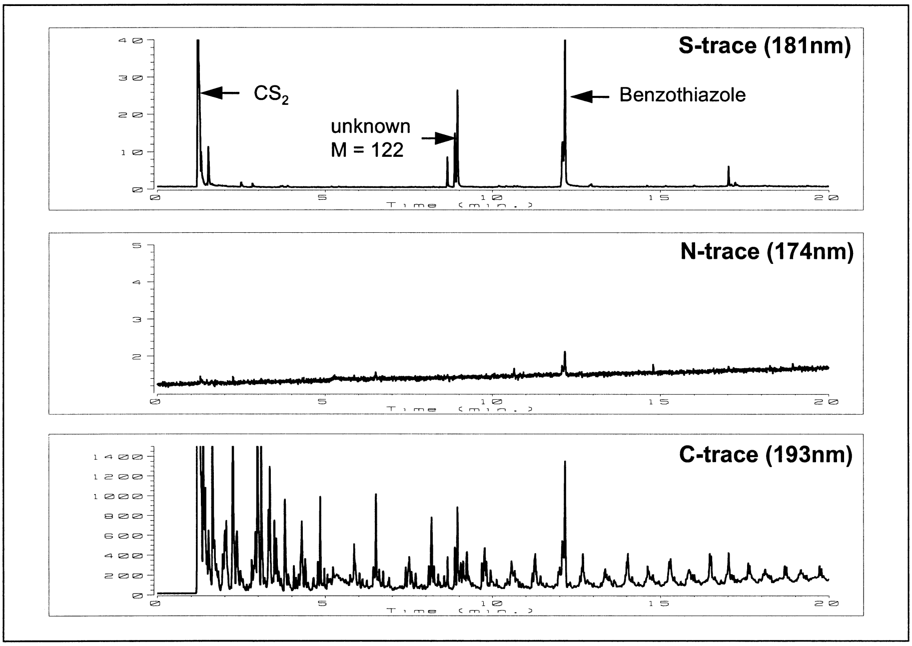

Fig. 3: Pyrolysis-GC/AED chromatograms of a typical EPDM rubber

Approach for Solutions

To characterise a rubber and its vulcanisation system all the presented analytical tools produce more or less useful results. The analyst chooses a selection of methods depending on his target. The results of each method represent bricks of a puzzle. Only the right combination of these results lead to an adequate solution of a given problem. Experience with the materials and analytical tools, access to appropriate infrastructure and extensive analytical databases help to reach even aims of high performance.

The schemes in Table 2 and Fig. 4 represent analytical approaches for the characterisation of the compositions and the vulcanisation systems of rubbers with unknown formulations. The presence of sulphur in a rubber is not sufficient to identify a sulphur vulcanisation system: Other sulphur containing additives as described in Table 1 can interfere. Only chromatographic methods can lead to a reliable statement as it is shown in Fig. 4.

The diversity of available rubber materials for strongly varying applications is immense. New designed specifications afford new compound formulations and also new polymers. Therefore it will be also a continuous challenge for expert analysts to support industrial research and development activities with outstanding analytical solutions based on the existing and new analytical tools.

Table 2. Analytical tools for the characterisation of rubbers

material for analysis	**analytical tools:**		
	coarse composition	**fine composition**	**scientific aspects**
untreated material	TGA[a] S(qual)[a][d] XRF[a]	EA[b] (i.e. S(quant)[d]) colour reactions[d] EGA[d]	ESCA[f] TOF-SIMS[f]
solvent extract	IR[a]	TGA[b] TLC[b][d] GC[b][d], HPLC[b][d]	NMR[e]
residue of solvent extract	TGA[a] IR[a]	EA[b] (i.e. S(quant)[d] Pyr-GC[b][c][d] NMR[c]	NMR[e][g] RAMAN[a][c][g] XANES[g]
ash	IR[a]	RFA[b] EA[b]	XRD[e]

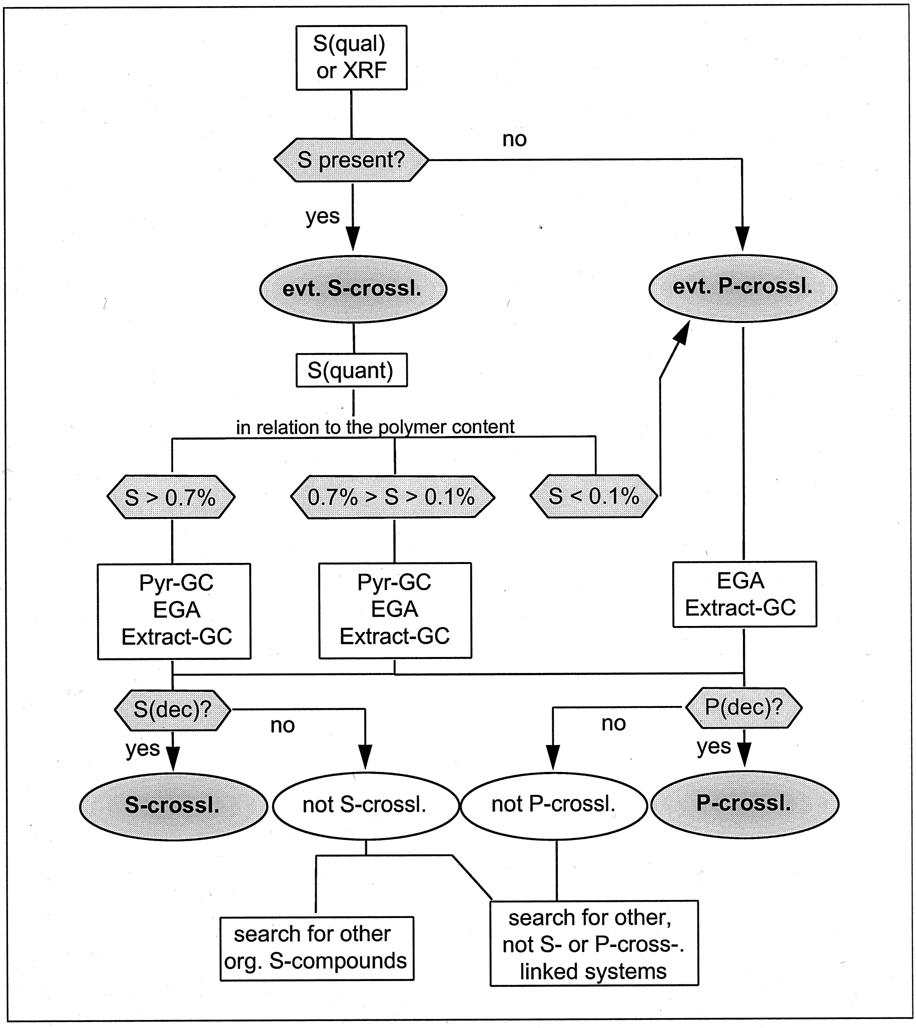

Fig. 4: Scheme to charaterise the vulcanisation system of rubbers

Legend for Table 2 and Fig. 4:

a) main components and composition of the material
b) details of components and composition of the material
c) analysis of blends and copolymers
d) characterisation of the vulcanisation system
e) molecular structure
f) surface properties
g) type of cross-linking bridges

Analytical tools:

S(qual) = qualitative proof of organic bound sulphur
S(quant) = quantitative determination of organic bound sulphur
EA = elemental analysis
IR = infrared spectrometry
RAMAN = Raman spectrometry
NMR = solid state ^{13}C nuclear magnetic resonance spectrometry
XFA = X-ray fluorescence analysis
XRD = X-ray diffraction
XANES = X-ray near edge absorption spectrometry 18-19)
ESCA = electron spectroscopy for chemical analysis
TOF-SIMS = time of flight secondary ion mass spectrometry
TLC = thin layer chromatography
GC = gas-chromatography coupled with suitable detector
HPLC = liquid chromatography
EGA = evolved gas analysis
Extract-GC = GC of solvent extracts
Pyr-GC = pyrolysis gas-chromatography
TGA = thermogravimetric analysis

Other abbreviations:

EPDM = ethylene-proylene-diene copolymer
S = sulphur
P = peroxide
(dec) = typical decomposition products observed with EGA or Pyr-GC
crossl. = cross-linked

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