

Intrinsic Sulphur Content of Carbon Black and its Relevance to Rubber Vulcanisate Analysis

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This paper describes work carried out to improve the accuracy of any reconstruction of formulation of a black-reinforced rubber article by taking into account the sulphur level associated with the carbon black used in its manufacture. The sulphur content of carbon black can vary from the parts per million level to over the percent level according to the method of manufacture and the feedstock used, and this can influence any calculation carried out to reconstruct the original formulation. The carbon black is recovered from natural rubber vulcanisates by pyrolysis under nitrogen and after removal of acid-soluble inorganic fillers, the residual sulphur content is determined by a standard furnace combustion followed by titrimetric estimation of the sulphur as sulphate. It has been shown for a series of carbon blacks of various sulphur contents recovered from both conventional cure and EV systems based on NR vulcanisates that this residual sulphur content equates to the intrinsic sulphur content of the virgin black.

The various types of sulphur referred to in this paper are defined as follows:

- Intrinsic sulphur: The sulphur which is present in carbon black as it is purchased from the supplier.
- Total sulphur: All the sulphur which is present in the sample.
- Combined sulphur: All that sulphur which cannot be removed by extraction using the prescribed procedure.
- Free sulphur: Elemental sulphur (S_8)
- Cure sulphur: The sum of the elemental sulphur and the sulphur present in the accelerators.

It is well known that the intrinsic sulphur content of a carbon black can vary from the parts per million level to percent level according

to the method of manufacture and the feedstock used in its manufacture¹. Intrinsic sulphur levels are usually given for the various grades of carbon blacks in manufacturers' literature but it is not made clear that the sulphur content is not linked to the black type, but rather to the feedstock material.

This paper presents an analytical method which enables the intrinsic sulphur content of the carbon black which has been recovered from a black-filled natural rubber vulcanisate to be determined so that sulphur associated with the cure system and thus the cure system itself can be assessed.

It must be stressed that the method has been validated only for use with natural rubber vulcanisates which are free of sulphur-containing inorganic fillers. If other polymers are present, the method would have to be validated by use of suitable control samples. Procedures are available for determining the non-inorganic sulphur content of vulcanisates in the presence of fillers such as lithapone and barytes. These have not been validated under the conditions of this method but should be applicable.

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EXPERIMENTAL

Two different natural rubber formulations, conventional and efficient cure systems were used for this investigation as shown in *Table 1*. The samples were extracted with acetone, dried and their bulk formulation checked by thermogravimetric analysis (TGA)² to ensure that the black loadings were accurately known. All the formulations were as specified to within 1 p.p.h.r.

TABLE 1. FORMULATIONS USED FOR MIXES

Compound	Amount (parts by weight)	
	Conventional cure	Efficient cure
SMR 10	100	100
Black (as below)	50	50
Zinc oxide	5	5
Stearic acid	2	2
Oil	2	5
Sulphur	2.8	0.5
CBS	0.6	2.5

Samples cured as 200 × 200 × 2 mm sheets at 150°C for 30 min

The carbon blacks used covered the range N110 to N880. Initially, they were tested to make sure that they conformed to their grades, the particle size being measured by two methods — light dispersion method of Davies and Kam³ and the iodine absorption method (ASTM D 1510). The results of these determinations are shown in *Table 2*.

Intrinsic, free and combined sulphur determinations were also carried out on each virgin black and the results are also shown in *Table 2*.

The test methods are described in greater detail below.

Sample Pre-treatment

The extraction was carried out according to ISO 1407; 'Determination of Solvent Extract', Method A being used. The weighed sample was placed in a Soxhlet type apparatus and extracted overnight, the solvent was removed from the extracted sample by heating in an oven at 100°C to constant weight. This method of extraction was also used for the virgin carbon blacks and *not* that given for carbon blacks in ISO 6209.

The dried sample was split into two parts; 1 g was pyrolysed in preparation for the total sulphur determination as described below and for a particle size estimation by either the light dispersion method or the iodine absorption method. The remainder of the sample was then available for the determination of the polymer/filler/ash ratios using TGA and polymer identification using pyrolysis - infra-red spectroscopy⁴, information necessary if the determined levels of sulphur are to be expressed as parts per hundred.

Sulphur Determinations

Total sulphur was determined according to ISO 6528-3; 'Determination of Total Sulphur, Furnace Combustion Method'. This has been used in these laboratories for many years but with a few minor changes. The most significant

TABLE 2. CHARACTERISATION OF CARBON BLACKS USED

Sample No.	Type	Nominal particle size (nm)	Determined size		Sulphur determination (%)		
			Light Abs	Iodine Abs	Intrinsic	Free	Combined
1	N110	11/19	17	15	0.90	—	0.91
2	N330	26/30	27	28	1.13	—	1.15
3	N550	40/48	44	44	1.57	0.01	1.60
4	N601	49/60	55	80	0.61	—	0.57
5	N880	100/200	110	150	0.75	—	0.79

is that, in the ISO method, the sample is moved forward slowly into the centre of the furnace to decompose the sample, whereas in the apparatus in use at MRPRA, a small electrical heater is attached to the combustion tube outside the furnace entrance. By placing the sample in this heated zone, it is possible to view the sample decomposition and thus maintain a better control of it.

Combined sulphur was determined by exactly the same method as that used for total sulphur except that the determination was carried out on the dried extracted material. The combined sulphur value has to be corrected for the amount of extract before it can be related to the original sample weight.

Free sulphur was determined according to ISO 7269. The method is based on the extraction of sulphur with acetone and its subsequent reaction with a copper gauze to form copper sulphide. This is converted to cadmium sulphide which is titrated against standard iodine solution.

Pyrolysis of Vulcanisates

Pyrolyses were carried out as described by Davies and Kam³. After pyrolysis, the residue was treated with nitric acid (30%) to remove any soluble inorganic fillers present, washed thoroughly with distilled water until all the acid had been removed (neutral to litmus paper), and dried in an oven at 100°C to constant weight. If weight losses continue, it suggests that the sample has not been washed free of nitric acid and oxidation is occurring. In this case, the whole pyrolysis procedure should be repeated.

RESULTS AND DISCUSSION

The five blacks, chosen at random from stocks held at MRPRA, showed widely differing levels of intrinsic sulphur which exceeded the range usually quoted¹. These results are given in *Table 2*.

No effort was made to analyse blacks of the same grade from a variety of sources, or

obtained over a period of time, as this was not relevant to this study. As already stated, it is accepted that the variations, are, at least in part, due to differences in feedstock. The results clearly indicate that the sulphur present in all the blacks is not in a form which can be extracted overnight with boiling acetone.

After pyrolysis of the uncompounded blacks, the total residual sulphur contents were again determined and these are given in *Table 3*. It is apparent that the intrinsic sulphur is not removed by heating to temperatures of at least 600°C.

TABLE 3. SULPHUR DETERMINATIONS ON RECOVERED CARBON BLACK^a

Black No.	Intrinsic sulphur (%)	Sulphur content (%)		
		Pyrolysed raw black	Conventional cure	Efficient cure
1	0.90	0.88	0.88	0.88
2	1.13	1.08	1.04	1.09
3	1.57	1.55	1.57	1.62
4	0.61	0.57	0.72	0.65
5	0.75	0.74	0.80	0.88

^aThese results are means of duplicate determinations with all results agreeing to within $\pm 0.04\%$.

Sulphur determinations on carbon blacks recovered after pyrolysis of conventional and efficient vulcanisates gave the results shown in *Table 3*. These suggest that the intrinsic sulphur is not involved to any significant percentage in crosslink formation, neither is any of the cure sulphur bound to the black in a form which cannot be removed by the isolation procedures described above. It thus appears that the intrinsic sulphur present in all the grades of black examined remains isolated and present during all rubber processing and analytical isolation procedures and is only liberated with combustion of the black. There is no reason to doubt that these conclusions will be valid for synthetic polyolefins, EPDM and probably for halo-polymers but this requires checking.

FORMULATION RECONSTRUCTION

It is important to consider just how the intrinsic sulphur content of carbon black can influence the calculation of the amount of cure sulphur added to a formulation and thus interpretation of the vulcanising system.

Total sulphur estimations on two vulcanisates both gave a value of 1.58%. TGA gave a polymer/black/ash ratio of 100/50/5 which, with an extract level of 3.1% (5 p.p.h.r.) gave a formula weight of 160. The sulphur levels of the recovered carbon blacks (*i.e.* the intrinsic sulphur contents) were measured at 1.62% and 0.72% which represent 0.506% and 0.225% respectively on the whole sample. The cure sulphur is thus, $1.58\% - 0.506\% = 1.074\%$ (1.72 p.p.h.r.) in the first case, $1.58\% - 0.225\% = 1.355\%$ (2.17 p.p.h.r.) in the second and 1.58% (2.53 p.p.h.r.) if no allowance is made for the intrinsic sulphur in the black.

It is quite obvious that whereas the uncorrected value is suggestive of a conventional cure, the results from the first case are more likely to represent an efficient cure system (0.6 p.p.h.r. elemental sulphur and 2 p.p.h.r. accelerator with 40%S) while in the second case, the suggested formulation would tend towards a semi-efficient system with 1 p.p.h.r. sulphur and 1.5 p.p.h.r. accelerator.

It would be unwise to quote these values to better than one decimal place but the identification and quantification of the accelerator

residues by high performance liquid chromatographic examination of the extract will enable a very precise description of the type of cure which can be obtained. It will be appreciated that the result will differ substantially from that obtained if no corrections are applied.

CONCLUSION

This work has shown how, by determining the amount of sulphur combined with the recovered carbon black (the intrinsic sulphur content), it is possible to give a much better estimate of the level of sulphur added during compounding. If this is combined with a knowledge of the accelerator system, it is possible to define completely the cure system.

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