Tracer Analysis of Elastomers: Curing Rates with Diphenylguanidine-³⁵S

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Diphenylguanidine (DPG)-pure gum vulcanisates are vulcanised various times (t) at 162°C, extracted for 48 h and chromatographed on Al_2O_3 . The initial fractions contain the free sulphur (Sf_1).

In most cases $\log \text{Sf}$ shows a linear relationship *versus* t indicating an approximate monomolecular reaction.

The investigated elastomers ranging from Butyl, Nordel, SBR, NR to *Cis*-butadienes give increasing rate constants (k) in the named order.

If k is plotted *versus* unsaturation the elastomers are grouped along two straight lines having different slopes.

The experiments were performed in the system:

Polymer	100 p.b.w.
Zinc oxide	1
Stearic acid	0—1
DPG	2
S	2
	<hr/> 106 p.b.w.

DPG was chosen partly for radiochemical reason, *e.g.* to avoid ³⁵S-exchange and partly as a not too efficient accelerator. For the same reason the amount of ZnO and fatty acid were kept low. In poly-isoprenes stearic acid can be omitted.

The vulcanisates can normally be characterised by the relation:

$$\log \text{Sf} = -k t + \text{constant} (\sim 0.3)$$

and principally by means of the single parameter k . The method can possibly be used for analysis of new polymers and for control of quality as well.

TECHNIQUE EMPLOYED

This is described elsewhere.¹ However, some few changes introduced later might be quoted here. The column for the chromatography had approximately a cross sectional area of 1 cm² and to the Al₂O₃ was added 3–4 % water. In all cases the retention of the 10 cm column should be controlled by standards, *e.g.* ³⁵S (0.5–2 mg/ml toluene) and TMT-³⁵S (tetramethylthiuramdisulphide 2–4 mg/ml toluene). The sulphur must cut sharply in the first 6 ml eluens, the TMT on the other side must follow later (10–15 ml). Before the evaporation of the acetone extract 15 ml toluene is added.

DATA

The total amount of soluble sulphur (*X*) in the toluene extract is determined by counting two samples having a volume of 0.5 ml, the blank (*Z*) without and the *Z*⁺-sample with addition of 1 ml standard ³⁵S-solution containing about 1 mg sulphur (*cf.* Table 1a).

5 ml scintillator solution * is added or when severe quenching occurs 0.25 ml extract may be taken in combination with 10–15 ml scintillator.

2–3 ml extract is used for the chromatogram which normally is eluted as 6–10 fractions having a volume of 2 ml. The 0–6 ml portion is counted again after addition of 1 mg ³⁵S.

The procedure is illustrated in Table 1a where the calculation is performed using R-168; Shell IR-305 as an example. Sf(*f*₁) denotes true free sulphur in 0–6 ml eluens whereas *f*₂ denotes sulphur in the following fractions from

Table 1a. 2.02^a ml extract of R-168, IR-305 vulcanised 4 min at 162°C. Fractions: 2 ml approximated colourless.

	fraction	cpm + standard	difference	ratio
Fraction	<i>Z</i>	<i>Z</i> ⁺	<i>Z</i> ⁺ – <i>Z</i>	<i>Z</i> /(<i>Z</i> ⁺ – <i>Z</i>)
1	23.454	112.148	88.694	0.26443
2	1.163	90.100	88.937	0.01307
3	691	80.148	79.457	0.00870
4	186			sum = 0.28620
5	97			× 13.06 ^b = 4.7378 mg S
6	47			sum: 6.836 ^c = 0.547 (<i>f</i> ₀) PHR
7	48			sum fractions (4–10) = 499 (<i>f</i> ₂)
				499 : 88.870 = 0.005615
8	44			~ 0.07333 mg S
9	31			~ 0.011 PHR
10	46			
Standard	88.870			

a) 25.03/2.020 = 12.391 aliquot

b) standard ³⁵S 1.054 mg × 12.391 = 13.06 mg

c) sample content of elastomer 683.6 mg

* 5 g POP + 0.5 g dimethyl-POPOP in 1 l pure toluene, *cf.* Ref.¹

Fig. 1. Free sulphur for various elastomers.
Cf. Table 2.

Fig. 2. Bound sulphur, total and chromatographed free sulphur for the compounds R-160 and R-169. Cf. Table 2.

6–20 ml. X , f_1 and f_2 are expressed as parts by weight per 100 g elastomer (PHR).

Table 1b gives the values of X , f_1 and f_2 together with the bound sulphur for the same isoprene rubber vulcanisates.

From Table 1b it is seen that $X > f_1$. It means that the extract contains S-compounds which are not free sulphur. The natures of the compounds are unknown but they may possibly be soluble polymer sulphides or sulphur compounds which are retained on the aluminium oxide. The "tail" f_2 is normally insignificant and possibly related to the complex decomposition of DPG during vulcanisation, recently treated by Dogadkin².

It is seen that the velocity of vulcanisation varies 100-fold passing from a *Cis*-butadiene to a low unsaturated butyl rubber. A comparison of the smoked

Table 1b. R-168, IR-305.

Vulcanised minutes at 162°C	S_b^a	X	$Sf(f_1)$	f_2
2	0.699	1.066	0.881	
4	1.08	0.664	0.547	0.011
8	1.57	0.351	0.283	0.006
16	2.01	0.0630	0.0329	0.003

^a) counted on the extracted solid samples using 4 untreated samples as standard (= 2.00 PHR).

Table 2.

Mix No.	Elastomers	PHR		$\frac{X}{\Delta \log X / \Delta t}$	f_1 $\log Sf_1$		$t_{\frac{1}{2}}^a$
		ZnO	stearic acid				
R-165	Cariflex Br-10P	1	1	-0.292	-0.329t	+ 0.579	1.8
-125	Cis-4	1	1	-0.227	-0.321t	+ 0.532	1.6
-130	Euoprene-Cis	1	1	-0.215	-0.242t	+ 0.364	1.0
-114	Deproteinised Rubber ^b	1	0		-0.155t	+ 0.276	1.8
-129	Smoked Sheets	1	0	-0.130			
-160	» »	1	1	-0.111	-0.182t	+ 0.456	2.5
-169	» + 1 part MB ^c	1	0	-0.189	-0.232t	+ 0.218	1.0
-168	Cariflex IR-305	1	0	-0.088	-0.102t	+ 0.176	1.7
-118	Ameripol CB	1	1	-0.102	-0.109t	+ 0.400	
-157	Synpol 8209	1	1	-0.066			
-133	Ameripol 1502	1	1	-0.045	-0.0643t	+ 0.410	6
-163	Philprene 1502	1	1	-0.030	-0.0338t	+ 0.281	9.5
-155	Synpol 8000			(-0.039)			7+
-161	Hycar 1000X-145	1	1	-0.0109	-0.0119t	+ 0.325	27+
-153	Nordel	1	1	-0.0073			20+
-158	Butyl NJ 035	1	1	-0.0028	-0.00284t	+ 0.255	90+
-171	Neoprene W	1	1	-0.0160	-0.0142t	+ 0.231	16.1

a) min, $t_{\frac{1}{2}}$, time to $Sf_1 = 50\% = 1.00$ PHR

b) by courtesy Drs. Bloomfield & Nielsen, Malaya

c) 2-mercaptobenzimidazole (Bayer's ASM MB).

sheet stocks 160 and 169 shows clearly the accelerating action of mercapto-benzimidazol, proving the usefulness of the method in compounding studies (*cf.* Fig. 2).

Table 3 contains some data for the elastomer used together with an estimate of unsaturatoin expressed as moles double bond per 100 g crude elastomer.

Table 3.

Elastomers	Polymer %	DB ^a /100 g	
Deproteinised Rubber (0.6 % protein)	98	1.44	Malayan Rubber Rubber Research Institute
Smoked sheets	94	1.38	
<i>Cis</i> -butadienes	99	1.83	Goodrich, Phillips, Shell, Anic.
SB-rubber 1502 ^b (23.5 % styrene)	92	1.30	Phillips, Goodrich, US
Synpol-8000 (45 % styrene)	92	0.94	Texus
Butyl NJ 035	99	0.015	Esso

a) moles bonds per 100 g rubber.

b) Styrene-butadiene rubber, cold polymerised, non staining antioxidant.

Fig. 3. Relation between rate constants k and unsaturation of elastomer. Cf. Table 2 and Table 3. SS = Smoked sheets; W = Neoprene W; DPR = Deproteinised rubber.

The relation between k and unsaturation is shown in Fig. 3 and the trends between fast and slow curing elastomers are seen.

CONCLUSIONS

In regard to the rapidity of the procedure, especially with the use of the Packard Liquid Scintillation Spectrometer, the method is well suited for routine work. Acetone extraction is the only limitation, otherwise it is possible to carry out 50 or more analyses a day provided only determination of total free sulphur is performed.

The run of the chromatogram takes about one hour and for routine work it is sufficient only to collect the first 6 ml in one vial. This procedure can be used for control of elastomers.

For scientific and compounding studies the chromatograms are completed and the method may be employed for the study of shifts of the rate constant k produced by a new component in a curing system, for example function of antioxidant and fillers at a given sulphur/accelerator level.

Finally, the labelled sulphur is now comparatively cheap. This is especially true when an original activity of 2 mC/g is used. This radio sulphur might be useful for 2 years at a 2 PHR level.

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