

Oxidation of Vulcanized Rubber

A procedure was recently described for estimating chain scission efficiently during the oxidation of rubber containing carbon black.¹ For oxidation at 140°, the efficiency was estimated to be approximately 0.11 moles scissions per mole oxygen, using an indirect calibration through measurement of volatile product yield. This estimate was obtained for rubber vulcanized with cumyl peroxide and containing a "medium processing channel" black.

Some forty separate vulcanizates have now been examined by the technique outlined in ref. 1, and scission efficiencies estimated from solubility changes. In the course of this work no important effect of temperature of vulcanization or of oxidation (in the range 120–160°), of the method of vulcanization, of the presence or absence of fillers, or the presence or absence of conventional antioxidants on the scission efficiency has been observed.

When the procedure from ref. 1 was followed exactly, a strong correlation between scission efficiency and crosslink density appeared to exist. Scission yields have now been recalculated making use of recent improvements in the estimation of the network crosslink density. Results for a set of samples containing carbon black are assembled in Table I. All samples contained 50 parts by weight of carbon black per hundred of rubber except that used in the experiment indicated by an asterisk. This one contained six parts.

The procedure for calculation of the figures in the last column of the table is as follows:

On the assumption that scission is random, scission yield is given by²

$$n \cong \nu (s + s^{1/2}) \quad (1)$$

where ν = chain density in the unoxidized network (corrected), and s = solubility in a good solvent.

The chain density of the unoxidized control ν_0 is obtained by using the Flory-Huggins relation as modified by Flory,³ with the value for μ of 0.38 for rubber in chloroform given by Bristow and Watson.⁴ This estimate is corrected for the effect of carbon black on swelling according to Smallwood,⁵ and the resulting value corrected for loose end effects and entanglements by the empirical relationship established by Mullins,⁶

$$\nu_0 = (\nu + 0.68 \times 10^{-4}) \left(1 - \frac{2 \times 10^{-6}}{\nu} \right) \quad (2)$$

For this correction the molecular weight of the polymer was assumed to be 10^6 . This is based on solution viscosity measurements with compositions prepared under the same conditions as the experimental samples, except that they contained no carbon black. The molecular weight-viscosity relation given by Mullins and Watson⁷ was used. There is evidence that the rate of breakdown during mixing at low temperature is the same for filled and unfilled compositions.⁸ Table I contains the values of chain density so derived from the given values of control swelling. Finally, the scission to oxygen ratio was obtained from the slope of plots of scissions vs. oxygen consumed.

Details concerning some of the compositions, particularly important for problems of oxidation mechanism, will be reported separately. Data in Table I show no evidence of

significant effect of vulcanization method on the scission efficiency as estimated from solubility changes. Further experimentation will be required to determine if the remaining slight trend of apparent scission efficiency with initial crosslink density is of mechanistic significance. Some of the variability in Table I is traceable to the unsuitability of a single μ value for all vulcanizates.

The mean scission efficiency derived from the table in-

TABLE I
Apparent Scission Efficiencies

Vulcanizing method, ^a black, temperature, °C.	Control swelling ^b	Chain density ^c	Oxidation temperature, °C.	Scissions oxygen
R, MPC, -80	10.15	0.52	150	0.07
P, MPC, 150	8.44	0.80	150	0.10
R, MPC, -80	8.40	0.85	140	0.08
P, MPC, 150	8.00	0.89	150	0.11
P, Graphon, 150	9.29	1.02	140	0.10
P, MPC, 157	7.47	1.05	150	0.13
T*, MPC, 120	9.42	1.05	140	0.10
S, MPC, 150	7.07	1.22	120	0.11
R, MPC, -80	7.03	1.23	150	0.08
S, MPC, 143	6.70	1.41	120	0.15
R, MPC, -80	6.60	1.46	140	0.11
T, MPC, 120	6.60	1.46	140	0.13
P, MPC, 150	6.56	1.49	140	0.13
S, MPC, 150	6.33	1.61	140	0.15
S, MPC, 140	6.27	1.65	140	0.13
P, HAF, 150	6.15	1.75	150	0.15
P, HAF, 150	6.16	1.75	150	0.16
S, MPC, 150	6.13	1.76	120	0.18
S, MPC, 150	6.08	1.80	120	0.13
P, MPC, 150	6.06	1.82	140	0.13
P, HAF, 150	5.99	1.86	150	0.16
P, MPC, 150	6.00	1.88	140	0.14
P, MPC, 150	6.00	1.88	140	0.13
S, MPC, 150	5.95	1.89	140	0.11
M, MPC, 155	5.80	2.02	140	0.30
P, HAF, 150	5.60	2.19	150	0.16
P, MPC, 150	5.14	2.69	150	0.14
P, MPC, 158	5.15	2.69	150	0.13
P, MPC, 120	4.48	3.96	150	0.23

^a Vulcanizing methods: MPC = medium processing channel black (Spheron 6, Godfrey L. Cabot, Inc.). HAF = high abrasion furnace black (Phylblack 0, Phillips Chemical Co.). Graphon = experimental black, Spheron 6 heated i.v. at 2700°; we are indebted to W. R. Smith of Godfrey L. Cabot Research Laboratories for this sample. R = radiation, in van de Graaf electron accelerator, 2×10^6 v. electrons, cooled in solid carbon dioxide. P = cumyl peroxide. T = "sulfurless" tetramethylthiuram disulfide plus zinc oxide. S = sulfur, zinc oxide, stearic acid, plus *N*-cyclohexyl-2-benzothiazyl sulfenamide (Delac S, Naugatuck Chemical Division, United States Rubber Company). M = methylolphenol (Super Berkacite 1001, Reichold Chemicals Corp.) plus zinc laurate.

^b Weight ratio, swollen (with chloroform) to unswollen corrected for filler.

^c Moles/10⁴ g. rubber.

cluding all data is 0.135 in the temperature range 120–150°. From published data,⁹ adjusted on the basis of the results of Mullins and Watson,⁷ the efficiency for raw rubber is estimated to be 0.16 at 140°.¹⁰

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