

"Directed Scission" in Rubber Vulcanizates

Horikx showed that main chain scission must occur in the degradation of sulfur vulcanizates of natural rubber by comparing the fractional solubility with the fractional loss in network chain density of the gel, after degradation.¹ Scanlan has extended the analysis used by Horikx to differentiate between random chain scission and scission at restricted sites in the network.² His results indicate that significantly different relationships between sol fraction and chain density loss are to be expected for the two courses of degradation. During investigations of rubber oxidation in these laboratories,³ we have routinely measured swelling as well as solubility of degraded vulcanizates. Results of some of these measurements for a number of kinds of vulcanized rubber are compared here with the predictions of the analysis by Scanlan.

Experimental

Essential features of the compositions of the vulcanizates used are given in Table I, which is also a key to the curves of experimental results in Figure 1. All compositions were

TABLE I
Compositions Used

Symbol in Fig. 1	Filler ^a	Vulcanizing agent	Vulcanization conditions	
			Time, hr.	Tem- pera- ture, °C.
○	None	Cumyl peroxide	2.5	150
⊙	None	Tetramethylthiuram disulfide	6	120
⊖	None	Accelerated sulfur	0.5	143
●	Graphon	Cumyl peroxide	2.5	150
●	Silica	Cumyl peroxide	2.5	150
●	MPC, HAF	Cumyl peroxide	2.5	150
●	MPC	Dimethylol phenol	4	155
●	MPC	Accelerated sulfur	0.5	143

^a Fillers used were: Graphon, an experimental deoxygenated carbon black, supplied by W. R. Smith, Godfrey L. Cabot Co.; silica in the form of Hi-Sil 233, Columbia-Southern Chemical Co.; MPC as Spheron 6, Godfrey L. Cabot Co.; HAF was Philblack O, Phillips Chemical Co.

prepared from commercial materials, including the required auxiliary ingredients for a conventional formulation of each type of vulcanizate. Fillers, where used, were about 20% by volume. The accelerator in accelerated sulfur compositions was either benzothiazolethione (MBT) or an MBT-sulfenamide. Compositions were assembled on laboratory mills and calendered 0.01 in. thick. Vulcanization with peroxide and with dimethylol phenol was done *in vacuo*, with sulfur in a press.

Some oxidation experiments were made in an apparatus, described previously,⁴ in which oxygen circulates continuously over the sample. Others were made with a simple device using a commercial aluminum testing block. In it oxygen absorbed was measured volumetrically at a con-

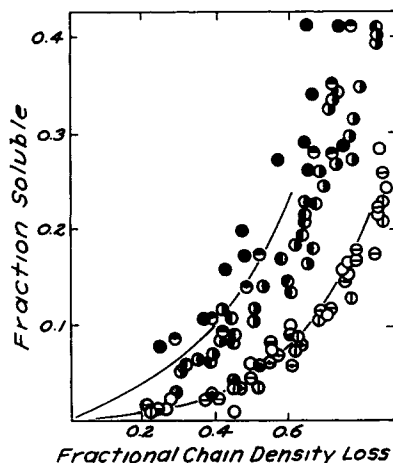


Fig. 1. Sol fraction as a function of gel network chain density loss. Upper solid curve theory for random chain scission, lower curve for "directed scission" at crosslinks.² See Table I for symbols.

stant pressure of one atmosphere. Barium oxide was used to absorb volatile products. The oxidation temperature ranged from 120 to 150°C., being chosen to give convenient rates of oxidation. Some samples were extracted in various ways before oxidation, others were not; no effect of extraction was observed, and no distinction is made between results for extracted and unextracted samples in the data of Figure 1. Antioxidants were added to the cumyl peroxide gum vulcanizates by infusion after vulcanization and before oxidation. This improved the reproducibility, compared with results for antioxidant-free samples.^{5b} Added antioxidant was not needed for the other samples. Solubility and swelling in chloroform were determined by weighing;^{5c} weights were corrected for the presence of filler. Chain densities were calculated in the usual way.⁶ No corrections for molecular weight, for entanglements, or for restriction of swelling by filler were applied for this comparison.

Results

The results of the degradation experiments are summarized in Figure 1 in which the curves derived from the theoretical analysis⁷ are sketched in. The solubility and chain density data from degraded gum vulcanizates and from the vulcanizate containing a nonreinforcing filler are in agreement with one another, the method of vulcanization having no effect. The data from vulcanizates containing reinforcing fillers, although showing more scatter, are also in reasonable agreement with each other, independently of the method used for vulcanization.

Two points concerning these results appear to be important.

(1) The experimental method does not show any significant difference in mechanism of degradation of vulcanized rubber conditioned by the nature of the crosslinking in the vulcanizate.

(2) *Reinforcing* fillers have a specific effect on the solubility/chain-density curves.

There is no evidence from other sources to suggest that the effect of fillers involves a difference in degradation mechanism; it must be an artifact of the experiment, de-

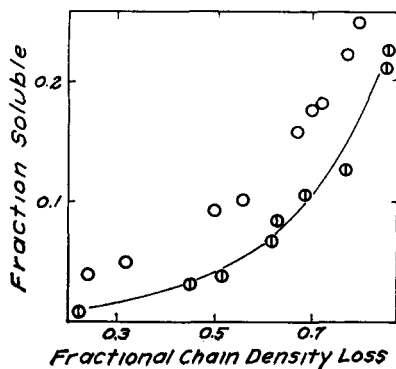


Fig. 2. Effect of degradation on sol/chain-density relation for tetramethylthiuram disulfide vulcanizate: (⊙) data from Fig. 1 for undegraded vulcanizate; (O) data for samples leached at 80° C. in 20% 2-ethylhexanoic acid in benzene before oxidation. Solid line is theory for "directed scission."

pending on the filler-rubber interaction. Two ways to observe a high solubility for a given extent of network degradation are known. Very readily oxidized samples often are oxidized inhomogeneously. This is frequently observed with peroxide gum vulcanizates, but is unlikely to be the explanation for the present results, since carbon blacks are antioxidants in peroxide vulcanizates. The second way to observe apparently high solubility is to use a partially degraded starting material. This is illustrated in Figure 2 for a TMTD vulcanizate; it has been described by Morton, Allen, and Gates.⁸ A possible explanation of the curve for filled compositions may be, therefore, that there is extensive degradation of the polymer during milling in the presence of reinforcing fillers, previously unrecognized. All of the compositions used in the work reported here were prepared by a "low hysteresis" process,⁹ which develops the maximum amount of covalent bonding to filler. This may have led to mechanical degradation, although no such effect has been detected in previous studies¹⁰ of black masterbatch milling.

Although data for the gum vulcanizates appear to fit the predicted curve for "directed scission," independent evidence will be required before it can be concluded that non-random degradation occurs. The theoretical curve applies to a network which initially has no free ends and is without entanglements; neither of these conditions is true of the actual networks.

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Role of Diffusion in Antiozonant Action

INTRODUCTION

The cracking phenomenon exhibited by stretched rubbers exposed to ozone has been the subject of recent physical studies.¹ It was found that certain "antiozonants," namely, the *N,N'*-dialkyl-*p*-phenylenediamines, increased the critical stress necessary for crack growth to occur.²

It has been suggested by Cox³ that such materials confer protection by competitive reaction with ozone, the antiozonant consumed at the surface of the rubber being replenished by diffusion from the bulk. This process has been termed "scavenging."

It has been inferred previously, from studies of the nature of the protection conferred by *N,N'*-dioctyl-*p*-phenylenediamine (DOPPD) that scavenging is not the operative mechanism.²

In support of this conclusion, the diffusion rate of DOPPD to the surface of a natural rubber vulcanizate has now been calculated and compared with the rate of incidence of ozone under conditions where the antiozonant is observed to be highly effective.

EXPERIMENTAL DETERMINATION OF THE DIFFUSION COEFFICIENT OF DOPPD IN NATURAL RUBBER

A sheet of vulcanized natural rubber, about 6 cm. square and ca. 0.08 cm. thick was immersed in DOPPD. The uptake (M_t) of DOPPD was determined as a function of time, until equilibrium swelling (M_∞) was attained. Classical diffusion theory⁴ shows that until equilibrium is approached:

$$M_t/M_\infty = 2(Dt/\pi l^2)^{1/2}$$

where D is the diffusion coefficient and $2l$ is the thickness of sheet. Figures 1 and 2 show that a plot of M_t against $t^{1/2}$ is substantially linear, from which the diffusion coefficient D can be calculated.

It should be realized that for a system such as a swelling rubber the diffusion coefficient increases as the polymer swells.⁴ Hence D is not a constant, and the above experiment determines an average diffusion coefficient \bar{D}