

Reclamation of Vulcanized Rubber by Chemical Degradation. XV. Degradation of Vulcanized Synthetic Isoprene by the Phenylhydrazine-Iron (II) Chloride System

INTRODUCTION

The phenylhydrazine-iron (II) chloride system is a good catalyst to reclaim unsaturated synthetic rubber vulcanizates at room temperature under atmospheric pressure.^{1,2} Utility of the products was also demonstrated.¹ The chemicals remaining in the products did not exert significant influence upon the thermal stability of the vulcanized reclaim.¹ The reclaiming process involved an oxidative degradation of vulcanized rubber by atmospheric oxygen, and the network chain underwent a severance reaction by the reagents in the following order of ease: polysulfide linkage > monosulfide linkage > carbon-carbon crosslink.³ The relationship of soluble fraction with decrease of effective network chain density during the degradation according to the theory of Horikx⁴ indicated that the severance of crosslinks dominated the main-chain scission in the degradation.³ There was, however, a gap in the experimental conditions between the mechanical study³ and the reclaiming process.^{1,2} That is, in the reclaiming studies,^{1,2} vulcanized rubbers were treated with the phenylhydrazine-iron (II) chloride system. On the other hand, in the mechanical study,³ iron (II) chloride was compounded with rubber before vulcanization, and the degradation was performed by soaking the vulcanizate in a benzene solution of phenylhydrazine. This technique was necessary to exclude the effect of oxygen. Therefore, we studied the mechanism of degradation of vulcanized rubber by the phenylhydrazine-iron (II) chloride system.

EXPERIMENTAL

Materials

We employed IR-2200 provided by Japan Synthetic Rubber Co. as the starting raw rubber. Commercial samples of rubber chemicals, iron (II) chloride, phenylhydrazine, benzene, methanol, and other chemicals were used without further purification.

Vulcanization

Three types of gum vulcanizates were prepared with the ingredients given in Table I. Symbols of these vulcanizates were used as in a previous paper of this series.³ Iron (II) chloride was not compounded with the rubber prior to the vulcanization.

TABLE I
Recipe for Vulcanization^a

Chemicals, phr	Type of vulcanizate		
	IR-S _X	IR-S ₁	IR-S ₀
Sulfur	1.5	—	—
Zinc oxide	5	5	—
Stearic acid	1	1	—
<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide	1.5	—	—
Tetramethylthiuram disulfide	—	3	—
Dicumyl peroxide (40C) ^b	—	—	2
2,2-Methylenebis-4-methyl-6- <i>tert</i> -butylphenol	1	—	—

^a Vulcanization condition: temperature, 140°C; time, 40 min.

^b 40%.

Degradation of Vulcanized Rubber

The vulcanized rubber was extracted with benzene for several days at 30°C and dried *in vacuo* at room temperature in order to remove the vulcanization residues including antioxidants. The degradation was performed at 30°C in air by soaking the vulcanized rubber in a mixture of 0.127 g iron (II) chloride and a specific amount (given in each figure) of phenylhydrazine, 12 ml methanol, and 288 ml benzene with stirring.

Physical Properties of Polymers

Swelling measurements were conducted by soaking vulcanized rubber in benzene at 30°C for 20 hr. After the soaking, the gel was obtained by drying the residual vulcanizates *in vacuo* at room temperature. The sol was determined as the difference in weight before and after the swelling experiments. The soluble fraction was expressed by $[\text{sol}/(\text{sol} + \text{gel})] \times 100(\%)$. Effective network chain density ν_e of the vulcanizates was determined using the modified Flory–Rehner equation.^{3,5} The value⁶ of 0.39 was used as an interaction parameter μ between solvent and polymer. Since this network chain density was calculated on the basis of the total amount of crosslinks, which included both chemical crosslinks and entanglements, the network chain density was evaluated on the basis of the actual number of chemical crosslinks according to the procedure of Mullins,⁷ expressed as ν_e' .

RESULTS AND DISCUSSION

Degradation of vulcanized synthetic isoprene rubber was performed by soaking it in a mixture of phenylhydrazine, iron (II) chloride, benzene, and methanol at 30°C with stirring. The ratio of decrease of ν_e' to the ν_e' before degradation, $(\nu_{e0}' - \nu_{et}')/\nu_{e0}'$, was plotted against the soaking time (Fig. 1). The decrease in the value of ν_e' was in the order $\text{IR-S}_X > \text{IR-S}_1 > \text{IR-S}_0$, as in the phenylhydrazine degradation of the vulcanizates compounded with iron (II) chloride.³ The network chain underwent a severance reaction by the phenylhydrazine–iron (II) chloride system in the following order of ease: polysulfide linkage > monosulfide linkage > carbon–carbon crosslink. However, the decrease in the effective network chain density observed in this work was much smaller when compared with those reported previously³ where iron (II) chloride was compounded with the rubber prior to vulcanization. This result shows that the iron (II) chloride compounded with the rubber prior to vulcanization considerably accelerated the degradation of the vulcanizate by phenylhydrazine.

Horikx correlation^{3,4} of the soluble fraction with the decrease in the effective network chain density for the degradation of vulcanized synthetic isoprene rubber was shown (Fig. 2). The figure shows a striking contrast to the previous results.³ That is, in the phenylhydrazine degradation of sulfur vulcanizate of synthetic isoprene rubber compounded with iron (II) chloride, the Horikx relation indicated that the severance of crosslinks dominated the main-chain scission.³ On the contrary,

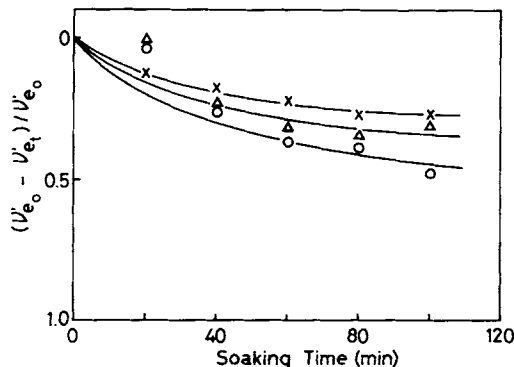


Fig. 1. Effect of soaking time at 30°C in a mixture of phenylhydrazine (0.01 ml), iron (II) chloride (0.127 g), benzene (288 ml), and methanol (12 ml) on the ratio of decrease of the effective network chain density for the degradation of vulcanized synthetic isoprene rubber: (○), (△), and (×) respectively denote degradations of IR-S_X, IR-S₁, and IR-S₀.

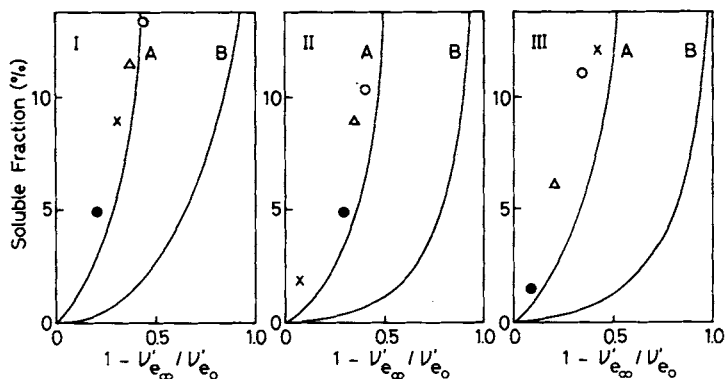


Fig. 2. Horikx correlation⁴ for the degradation of vulcanized synthetic isoprene rubber in a mixture of phenylhydrazine, iron (II) chloride (0.127 g), benzene (288 ml), and methanol (12 ml) at 30°C: A and B are theoretical curves for main-chain scission and severance of crosslinks, respectively. (I) IR-S_X, amount of phenylhydrazine: (O) 0.3 ml; (Δ) 0.03 ml; (×) 0.01 ml; (●) 0.005 ml. (II) IR-S₁, amount of phenylhydrazine: (O) 0.05 ml; (Δ) 0.02 ml; (×) 0.01 ml; (●) 0.015 ml. (III) IR-S₀, amount of phenylhydrazine: (O) 0.1 ml; (Δ) 0.05 ml; (×) 0.03 ml; (●) 0.01 ml.

Figure 2 shows that the main-chain scission dominated the severance of crosslinks in the degradation of vulcanized synthetic isoprene rubber by the phenylhydrazine-iron (II) chloride system. This result suggests that the iron (II) chloride compounded with rubber, prior to vulcanization, exerted a strong interaction with the crosslinks of the vulcanizates and accelerated the degradation of the vulcanizates by phenylhydrazine. On the other hand, in the degradation of vulcanized synthetic isoprene rubber by the phenylhydrazine-iron (II) chloride system, the reactive radicals mainly attack the main chain of the vulcanized rubber, resulting in the predominance of the main-chain scission over the severance of crosslinks.

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