[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XIII. The Molecular Weight of Sol Rubber

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE, ALVIN F. SHEPARD AND MARY W. RENOLL

A method is presented whereby the molecular weight of rubber has been computed from the results of chemical analyses. It consists in combining rubber and sulfur, then separating the reaction products by fractional precipitation into portions containing increasing amounts of sulfur. Analysis shows that the sulfur content of the second portion is twice that of the first, and that of the third three times that of the first. The simple assumption is then made that the successive portions contain definite compounds in which one molecule of rubber is combined with one, two and three atoms of sulfur, respectively. The computation of the molecular weight of rubber is thus made possible.

The experimental procedure is outlined as follows. Pure sol rubber hydrocarbon[1] mixed with tetramethylthiuram disulfide and zinc stearate is heated until approximately 0.06% sulfur is combined with the rubber. This material is subjected to repeated fractional precipitation from a mixture of alcohol and benzene[1] until no further separation takes place and the amount of combined sulfur is determined in the several fractions. The results appear in the tables.

Three successive components are thus isolated, with sulfur contents of 0.058 ± 0.003%, 0.116 ± 0.003% and 0.179 ± 0.003%, respectively. Assuming that they are the mono-, di- and trisulfur derivatives of rubber, the molecular weight of rubber can be computed as 55,859 ± 2800, 55,556 ± 1400, or 53,637 ± 700. Values between 54,337 and 54,156 are common to all three determinations. They correspond to 799 and 791 isoprene units in the rubber molecule.

The particular vulcanizate used in these determinations was selected from a variety of others as best adapted to the desired purpose. The results obtained with other experimental conditions are beyond the scope of the present paper.

As a corollary derived from the experimental results so far obtained, it may be concluded that, at least in its first stages, vulcanization should not be regarded as a linking of different rubber molecules by sulfur bridges. Intermolecular linkings would greatly increase the molecular weight, and cause a decrease of solubility out of proportion with that actually observed. Furthermore, a fractionation would then yield sulfurized compounds which could be represented successively by RS_0, R_2S_1, R_3S_2, . . . , $R_nS_{(n-1)}$, . . . , $R_\infty S_\infty$ (where R is the rubber molecule and S is a sulfur atom). In contradistinction, the experimentally obtained compounds are RS_0, RS_1, RS_2, RS_3. Consequently, intermolecular linkages cannot be accepted, within the scope of the experiments.

Experimental Details

A. Interaction of Rubber and Sulfur

Rubber (97 g.), tetramethylthiuram disulfide (3.63 g.) and zinc stearate (0.97 g.) were dissolved in benzene (2500 g.). The solvent was removed at room temperature under high vacuum. The resulting skin of rubber was cured *in situ* by heating the flask for thirty minutes at 100° in an oil-bath, after a ten-minute preheat at 95°. A sol fraction from sprayed latex[2] was used; all operations were performed in a carbon dioxide atmosphere, and all solvents were freed of air and saturated with carbon dioxide. This procedure was preferred because it eliminated milling and reduced contact with air, thus avoiding degradation.

B. Fractionation

The product was subjected to fractional precipitation,[1] and the fractions were analyzed for combined sulfur,[3] as shown in Table I.

TABLE I

PRIMARY FRACTIONATION

Fraction	Weight, g.	S, %	Solubility in C_6H_6
A-1	18.8	0.065	Sol.
A-2	11.7	.065	Sol.
A-3	9.3	.069	Sol.
A-4	5.2	.105	Sol.
A-5	6.6	.116	Sol.
A-6	9.3	.127	Sol.
A-7	11.6	.207	Partly sol.
B	13.3	.242	Insol.

Fractions A-1, A-2 and A-3 were combined and refractioned. Fractions A-4, A-5 and A-6 were similarly united and refractioned. Fraction

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(1) Midgley, Henne and Renoll, THIS JOURNAL, **53**, 2733 (1931).

(2) Midgley and Henne, *J. Phys. Chem.*, **36**, 2280 (1932).

(3) Wolesensky, *Ind. Eng. Chem.*, **20**, 1234 (1928).

B was finely cut and allowed to soak in benzene as long as soluble matter diffused out. This soluble material (2.8 g.) was added to fraction A-7 and was also refractioned. The results appear in Table II.

TABLE II

SECONDARY FRACTIONATIONS

Initial material	Fraction	Weight, g.	S, %	Solubility in C_6H_6	
A-1, A-2 and A-3	A_2-1	13.7	0.058	Sol.	$RS_1 = 0.0574\%$ S
	A_2-2	8.0	.057	Sol.	
	A_2-3	4.8	.056	Sol.	
	A_2-4	8.0	.043	Sol.	
A-4, A-5 and A-6	A_2-5	2.8	.115	Sol.	$RS_2 = 0.1153\%$ S
	A_2-6	3.9	.112	Sol.	
	A_2-7	8.1	.117	Sol.	
A-7 and part of B	A_2-8	4.0	.179		

C. Analytical Procedure

The finely cut rubber samples were extracted with acetone in a Soxhlet apparatus for twenty-four hours, swelled with benzene, soaked in alcohol and freed of inorganic sulfides.[4] Blank runs demonstrated that this treatment was adequate. The sulfur content[3] was determined by the procedure of Wolesensky. All results were corrected for parallel blank determinations.

Due to the limited amount of material available, double analyses were performed only in a few cases; with only one single exception the results checked within experimental error, and in the exceptional case, a third analysis secured the needed confirmation.

During the course of the fractionation it was noted that vulcanization was still progressing and also that traces of unreacted accelerator were removed by the solvents used in the fractionation. This explains why the total amount of combined sulfur was not constant after each fractionation. As the theoretical reasoning is based only on the final results, when the sulfur concentration no longer changed, it is not affected by these details.

Conclusion and Summary

Partially vulcanized rubber has been fractionated into components in which rubber is combined with increasing amounts of sulfur. The analyses of these fractions concur to indicate a molecular weight of about 54,000 for the particular sample of rubber used. Specimens of varied origin, can thus have their molecular weight measured by strictly orthodox chemical means.

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(4) Stevens, *Analyst*, **40**, 275–281 (1915).

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Natural and Synthetic Rubber. XIV. A Structural Formula for Ebonite

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The ninth paper of this series[1] reported a list of compounds obtained by the pyrolysis of ebonite and stated that their correlation might elucidate the constitution of ebonite.

The compounds positively identified, and their relative amounts, were benzene, <0.5; 2-methylthiophene, 10; toluene, 1; 2,3-dimethylthiophene, 50; 2,4-dimethylthiophene, 10; *m*-xylene, 50; 2-methyl-5-ethylthiophene, 240. Moreover, it was established definitely that thiophene itself, and those of its homologs with less than eight atoms of carbon other than the ones just mentioned, were positively absent.

The above compounds are obtained by themselves only when ebonite is destructively distilled. Mixtures of raw rubber and sulfur yield other isomeric forms as does the reaction of sulfur with the pyrolysis products of raw rubber. For example, ebonite yields only 2-methylthiophene, while isoprene and sulfur yield only 3-methylthiophene;[1] a mixture of raw rubber and sulfur yields both isomers. Hence the compounds actually isolated were derived from fragments of the ebonite molecule and not merely from fragments of the rubber molecule with sulfur subsequently attached.

The identified decomposition products accounted for only 1.1% of the original material and it is therefore possible that the type of sulfur linkage developed in the following reasoning is not the only one present.

I. Only four out of the twenty-one possible thiophenes of substantially equal stability with less than eight carbon atoms were produced. Random linking of small fragments after extreme

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(1) THIS JOURNAL, **54**, 2953 (1932).