PREPARATION OF SULPHUR, SULPHUR AND CARBON CONTAINING POLYSILOXANE ELASTOMERS

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Introduction

The skeleton of the silicone elastomers is usually formed by a polysiloxane chain containing methyl groups on the free valencies of the silicon atoms. There are two possibilities of vulcanization, depending on the feature of the terminal groups of the polysiloxane chain. If these are methyl or vinyl groups, the crosslinking can be achieved by so-called hot vulcanization, using different organic peroxides, sulphur or active sulphur compounds (Se, Te, dithiocarbamates, guanidines etc.) and pressure. In this case the silicone rubber contains the sulphur in the crosslinks [1, 2, 3]. If the terminal groups of the polysiloxane chains are more reactive (e.g. OH, alkoxy or acetoxy) the silicone rubber can be synthesized by means of thiurames or mercaptans in the presence of catalysts (e.g. dibutyl-tin-dilaureate) at room temperature [4]. The first silicone polymer, containing polysulphide links in the siloxane chain was synthesized by NASIAK and POST [5], who did not expose this polymer to vulcanization. PLUDDEMANN [6] built up a crosslinked polysulphid elastomer by the help of the branched groups of the polymer, hydrolysed by the moisture of air.

In our own experiments the synthesis of silicone elastomers, containing sulphur as well as sulphur and carbon in the polysiloxane chain in distinct sequencies, had been aimed at. The synthesized elastomers were characterized by their average molecular weight, their intrinsic viscosity and by their terminal group analysis. Thereafter vulcanization was done at room temperature, and the mechanical properties of the resulting rubbers were tested. The obtained results were compared with test data on pure polysiloxane elastomer, vulcanized under similar conditions.

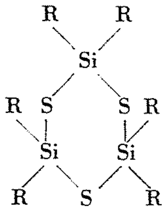
Experimental part

In our experiments elastomers had been synthetized containing

1. $-Si-S-Si-$
2. $-Si-C-S-Si-$
3. $-Si-C-Si-S-Si-$ and
4. $-Si-C-Si-$

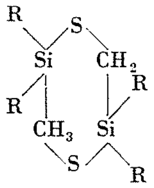
units. The ratio between these units (E) and the silicon atoms of the polysiloxane chain were chosen as E/Si = 1/20; 1/50; 1/100 and 1/150. The hetero units mentioned above were built in into the polysiloxane chain by the following compounds:

1)



Hexamethyl-cyclotrisilthiane
($R = CH_3$)
Bp_{38}: 151,5—153,5°

2)



2,2,5,5-Tetramethyl-2,5-disila-1,4-dithia-cyclohexane
($R = CH_3$) m.p.: 82—83°

3) $(Cl—CH_2—Si(CH_3)_2)_2S$ Bis-(chloromethyl-dimethylsilyl)-sulphide Bp_{10}: 80—81°

4) $Cl—CH_2—Si(CH_3)_2—Cl$ Chloromethyl-dimethyl-chlorsilane.

For the synthesis of the hetero-siloxane elastomers two routes can be used:

A) Starting from the heteroatom containing silicon compound an oligomer has to be produced first (e.g. by the way of Grignard reaction, addition etc.) and this has to be copolymerized with cyclic siloxanes in the presence of catalysts [7, 8].

B) Starting from cyclosiloxane a prepolymer is to be made and this has to be joined with a heteroatom containing silicon compound in the presence of a catalyst. This method is used in the industrial production too [9].

In the synthesis of the silicone elastomers containing heteroatoms we used always this second method. Starting from octamethyltetracyclosiloxane a prepolymer was formed in the presence of 3% concentrated sulphuric acid as catalyst, then the appropriate heteroatom containing silicon compound was added in the required ratio, and the reaction mixture was stirred at room temperature until the viscosity of the polymer remained constant. The elastomer was resolved in ether, the solution was deacidized by washing with sodium bicarbonate, dried ($CaCl_2$) and evaporated. Traces of the solvent and oligomers were removed by vacuum distillation. The remaining silicone elastomers had following properties:

Table I

Properties of the silicone elastomers

Type of unit*	Average M. weight	Viscosity	Terminal group			S/Si rate
			OH	SH	Cl	
SiS	35 100	0.200	+	—	—	1 : 20
SiS	41 100	0.222	+	—	—	1 : 50
SiS	50 000	0.254	+	—	—	1 : 100
SiS	84 000	0.363	+	—	—	1 : 150
CS	39 400	0.216	+	+	—	1 : 20
CS	147 000	0.514	+	+	—	1 : 50
CS	182 000	0.593	+	+	—	1 : 100
CS	178 000	0.584	+	+	—	1 : 150
C	9 800	0.086	+	—	+	1 : 20
C	24 000	0.156	+	—	+	1 : 150
CSiS	20 000	0.136	+	—	+	1 : 20
CSiS	42 000	0.225	+	—	+	1 : 150
NG	20 500	0.140	+	—	—	0

* The abbreviations used in this table are: SiS = —Si—S—Si—; CS = $—CH_2—S—Si—$; l = $—Si—CH_2—Si—$; CSiS = $—CH_2—Si—S—Si—CH_2—O—$; and NG = —SI—O—Si—.

Vulcanization of the elastomers

The synthetized silicone elastomers, containing heteroatoms in their skeleton underwent vulcanization at room temperature, using tetraethoxy-silane as crosslinking agent and dibuthyl-tin-diacetate as initiator. The composition of the reaction mixture, used for the vulcanization was the following: 100 g elastomer, $2.24 \cdot 10^{-2}$ mol tetraethoxy-silane and $9.25 \cdot 10^{-4}$ mol dibuthyl-tin-diacetate. The elastomers of the SiS and CS type became rubbers after 24 hours with exception of the CS 1 : 20 type, which became just a gel. The same happened to the elastomers of the CSiS type, while the elastomers containing $-CH_2-$ groups in the polysiloxane chain remained unchanged. The SiS and CS type rubbers were tested for elasticity and solvent resistance.

Discussion

The vulcanization experiments of the different polysiloxane elastomers showed this process as well as the features of the resulting products to be strongly terminal-group dependant. The reactivity of these terminal groups towards tetraethoxy-silane determines the vulcanization rate. For instance, if the terminal groups of the elastomer are hydroxyls — as in the case of the SiS elastomer — the vulcanization process is the same as described for the normal silicone rubbers, vulcanized at room temperature [9]. Changing part of these terminal groups to —SH groups — as in the CS type elastomer — the vulcanization rate decreases and if the ratio of SH to OH groups will reach 2 : 1, no rubber result. The fact that in the case of the CSiS type elastomer only a gel formed indicated the low reactivity of the chloromethyl terminal groups, insufficient for the elastomer to establish crosslinks with tetraethoxysilane. The reduced reactivity of the chloromethyl groups is indicated even by the lower average molecular weight of the elastomer, proving that all the

Table II

Elasticity testing of silicone rubbers

%	Type of rubber							
	CS-50	CS-100	CS-150	SiS-20	SiS-50	SiS-100	SiS-150	NG
Elasticity	10.9	40.3	39.5	65.9	79.2	74.2	74.6	76.5
Rel. hyster	89.1	59.7	60.5	34.1	20.8	25.8	25.4	23.5
Perm. set	78.0	39.5	38.5	10.5	4.0	9.5	6.5	9.5
3 hours at 150°								
Elasticity	—	32.2	26.0	67.1	81.0	75.6	72.2	76.5
Rel. hyster.	—	67.8	74.0	32.9	19.0	24.4	27.8	23.5
Perm. set	—	65.0	65.0	7.0	5.0	8.5	5.5	7.5
6 hours at 150°								
Elasticity	—	—	—	81.1	81.0	75.6	78.2	75.0
Rel. hyster.	—	—	—	18.9	19.0	24.4	21.8	25.0
Perm. set	—	—	—	6.0	5.0	8.5	7.5	7.5

chloromethyl groups were present at terminal positions, preventing the polysiloxane chains from further condensation or crosslinking.

Comparative study of the SiS and CS types, and the pure polysiloxane rubber proved that the sulphur content of the Si—S—Si units had a favourable influence on elasticity. The elastic properties of the different rubbers were investigated before and after being heated to 150 °C for 3 and 6 hours, respectively. The data proved the benefit of having built in sulphur into the silicone rubber, as in the series of the SiS type rubbers the elasticity increased parallel to the sulphur content. On the other hand, the same investigations on the series of the CS type rubbers showed that the $-\mathrm{Si}-\mathrm{CH}_2-\mathrm{S}-\mathrm{Si}-$ units significantly diminished the elasticity of the polymers after a treatment at 150 °C for 3 and 6 hours, respectively.

Table III

Swelling of the rubbers (%) in ethanol

Time (hours)	Type of the rubber							
	CS-50	CS-100	CS-150	SiS-20	SiS-50	SiS-100	SiS-150	NG
2	1.70	1.63	1.52	1.18	1.96	1.95	2.26	1.48
24	2.66	2.42	2.04	1.98	2.52	3.11	3.13	2.44
96	1.82	2.43	1.63	0.05	1.78	2.40	2.50	1.65
170	1.21	2.55	0.82	0.49	1.18	1.69	2.35	0.86

Table IV

Swelling of the rubbers (%) in acetone

Time (hours)	Type of the rubber							
	CS-50	CS-100	CS-150	SiS-20	SiS-50	SiS-100	SiS-150	NG
2	25.7	25.9	22.9	20.4	23.0	23.1	23.2	18.5
24	28.0	24.5	24.3	22.4	24.5	26.3	24.8	24.4
96	24.7	20.0	21.2	16.4	20.0	22.4	22.5	20.6
170	22.7	16.5	17.7	15.2	15.0	19.5	18.5	16.0

Table V

Swelling of the rubbers (%) in toluene

Time (hours)	CS-50	CS-100	CS-150	SiS-20	SiS-50	SiS-100	SiS-150	NG
2	278	236	213	144	125	141	150	127
24	739	725	650	309	297	339	335	292
96	—	956	786	319	324	344	338	317
170	—	1074	794	295	316	361	319	302

The solvent resistance of the rubbers was studied for three solvents: ethanol, acetone and toluene. All of them can have two simultaneous effects: partly they will swell the rubber by penetration, and partly they will dissolve the polymers of lower molecular weight. As this two effects entrain opposite changes in the weight, the mass change of the test pieces will be their resultant. If the swelling surpasses the dissolution, there will be a positive change in the weight, and in opposite case there will be a loss of it.

Evaluation of these data led to the conclusion, that the heteroatoms built into the polysiloxane chains did not significantly alter the solvent resistance, as against the $-Si-CH_2-S-Si-$ unit, which extremely reduced the toluene resistance of the rubber.

Summary

The synthesis of elastomers, containing sulphur as well as sulphur and carbon as heteroatoms in the polysiloxane chains is described. The different elastomers were vulcanized in the presence of tetra-ethoxy-silane as crosslinking agent, and dibuthyl-tin-diacetate as initiator. The elasticity and the solvent resistance of the resulting rubbers to ethanol, acetone and toluene were investigated. A correlation was established between the sulphur content and the properties of the different rubbers.

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