

Hydrosilylation Crosslinking of Silicone Rubber Catalyzed by Bis(1,5-cyclooctadiene)di- μ,μ' -chlorodirhodium

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SYNOPSIS

Hydrosilylation vulcanization of addition silicone rubber catalyzed by bis(1,5-cyclooctadiene)di- μ,μ' -chlorodirhodium at 150°C was studied. The course of vulcanization, rubber network density, and mechanical properties of the vulcanizate are discussed with respect to the structure and molecular weight of the reactive groups of telechelic and internal vinylmethylpolysiloxanes and crosslinking methyl (hydrogen) dimethyl siloxane copolymers. Molecular weights of the polysiloxane components as well as the ration of unsaturated and Si-H groups were optimized. The results are in agreement with the theory of rubber elasticity of polymer networks and show wide application possibilities of the catalyst used.

INTRODUCTION

Silicone rubbers crosslinked by a hydrosilylation reaction have become increasingly important in technical practice.¹⁻⁵ Their growing popularity is mainly due to their excellent electroinsulating properties and resistance to water, weather conditions, and elevated temperatures. There is a possibility of widely influencing the character of vulcanizates by the choice of the catalyst, of both the unsaturated and the H-components, and their mutual proportion.

In view of these facts, in the framework of our systematic studies of hydrosilylation crosslinking, we have subjected these factors to a detailed study.⁶⁻⁸ Recently we have found⁶ that the Rh(I) complexes, mainly bis(1,5-cyclooctadiene)di- μ,μ' -chlorodirhodium, are very effective catalysts for hydrosilylation crosslinking of polysiloxanes. Their activity is almost the same as platinum systems. Their main advantage is the unusually long shelf life of the prepared vulcanization mixture at room temperature and excellent catalytic properties at higher temperatures, and thus they are becoming the catalysts of choice for transfer molding applications.⁸

The behaviour of these Rh(I) complexes, however, has been tested only in commercial mixtures containing another branched polysiloxane besides the unsaturated telechelic vinylpolysiloxane and the polyfunctional H-polysiloxane. In order to extensively test the application possibilities of the most promising bis(1,5-cyclooctadiene)di- μ,μ' -chlorodirhodium, the course of vulcanization, density of polymer network, and mechanical properties of the vulcanizate were studied in the present study with respect to the structure and molecular weight of polysiloxanes as well as concentration and position of the reactive groups of the unsaturated and crosslinking components. In order not to distort the results with interfering factors, neither a filler nor a branched unsaturated component were added to the studied mixtures, and the prepared vulcanizates were studied from the point of view of their agreement with the theory of rubber elasticity.

EXPERIMENTAL

Materials

Solvents (Lachema, Brno) and organosilicon monomers (Lachema, Kolín) were dried prior to use in a standard manner and then distilled in an argon

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Table I Preparation and Properties of Vinylmethylpolysiloxane (Component A)

Denotation	Reactant ^a				CH ₂ = CH(CH ₃) ₂ SiO— (wt %)	Mean Viscosity Molecular Weight (g mol ⁻¹)	Iodine Value
	D ₄ (g)	M ₂ ⁱ (g)	Lewatit (g)				
1A	1600	15	60		0.73	34,000	2.15
2A	1600	6.7	80		0.39	57,100	1.15
3A	1500	4	75		0.28	79,900	0.82
4A	690	b	35		0.90 ^c	33,200	2.65

^a D₄ = octamethylcyclotetrasiloxane; M₂ⁱ = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane.

^b = 5.7 g hexamethyldisiloxane + 6 g tetramethyltetravinylcyclotetrasiloxane.

^c = CH₂ = CH(CH₃)Si(O—)₂ group.

atmosphere. Bis(1,5-cyclooctadiene)di- μ, μ' -chlorodirhodium was prepared by the reported procedures.⁹ Lewatite (sulphonated styrenedivinylbenzene resin) was dried at 95°C/2 kPa for 3 h. Mean viscosity molecular weights were determined by measuring the flow times of diluted toluene solutions of polymers using an Ubbelohde viscometer. They were calculated in the usual manner using the Mark-Houwink equation. Vinylmethylpolysiloxanes (component A) were prepared as follows: A mixture of octamethylcyclotetrasiloxane, tetramethyldivinyldisiloxane or tetramethyltetravinylcyclotetrasiloxane and Lewatite was equilibrated at 85°C for 2 h, stirred intensely, and afterwards filtered off and demonomerized at 150°C and a pressure of 1 kPa for 3 h. Components B were prepared in a similar manner by the equilibration of octamethylcyclotetrasiloxane hexamethyldisiloxane and methyl-(hydrogen)polysiloxane at 100°C. The properties of the reaction components and of the prepared polymers are listed in Tables I and II.

Preparation of Vulcanizates and their Evaluation

Vulcanizates were prepared by mixing A and B components in proportions stated below, under a catalytic action of Rh₂(C₈H₁₂)Cl₂ solution in chloroform.⁵ Catalyst concentration in the vulcanization mixture was 7 ppm reduced to rhodium. Vulcanization of test plates proceeded in a press at a temperature of 150°C for 30 min. One part of the plates was subjected to postvulcanization at 200°C for 4 h.

Vulcanizates were evaluated by determining tensile strength, ductility, and hardness according to Czechoslovak standards ČSN 62 1436 and ČSN 62 1431. In addition to mechanical properties, the concentrations of extractable portions, sols, and molecular weights of network chains, M_c , were measured. The initial values for calculation of these data were obtained by means of equilibrium swelling in toluene at room temperature. To calculate M_c , the Flory-Rehner equation¹⁰ (interaction parameter 0.465) was employed. The amount of sol was cal-

Table II Preparation and Properties of Methyl(hydrogen)polysiloxanes (Component B)

Denotation	Reactant ^a				Mean Viscosity Molecular Weight (g mol ⁻¹)	Active ^b H (wt %)
	D ₄ (g)	H-Polysiloxane (g)	M ₂ (g)	Lewatit (g)		
1B	795	290	55	80	2800	0.365
2B	630	94.5	18.1	70	6000	0.184
3B	718	107	2.2	70	31,000	0.181
4B	795	47	5	70	32,900	0.085
5B	735	27	0.8	70	47,800	0.050

^a D₄ = octamethylcyclotetrasiloxane; H-polysiloxane (CH₃)₃†O—Si(H)(CH₃)—_n OSi(CH₃)₃ containing 1.6% active H average of n = 36; M₂ = hexamethyldisiloxane.

^b = hydrogen in the form of Si—H bond.

culated from the weight differences of test samples prior to swelling and after desiccation of toluene.

RESULTS AND DISCUSSION

Preparation of Unsaturated and Crosslinking Components

The above described preparations are very simple and reproducible, and as seen from the data presented in Table I, by altering the mutual proportion of octamethylcyclotetrasiloxane and tetramethyldivinylsiloxane, the mean molecular weight of the prepared telechelic polymers could be controlled (1A to 3A). Practically the same results have been achieved also in replacing tetramethyldivinylsiloxane by diphenyldimethyldivinylsiloxane.¹¹ According to gel chromatographic analysis all polymers exhibited molecular weight distributions typical for equilibrated polysiloxanes and only a slight amount (about 10 wt %) of volatile fractions. In a similar way, an unsaturated polymer containing reactive centres (methylvinylsiloxy groups) in the polymer chain was prepared for comparison, which however, did not prove suitable as a component of silicone rubber.

The prepared methyl(hydrogen)polysiloxanes (Table II) also exhibited a very narrow distribution of molecular weights and a slight amount of volatile fractions. In the preparation of crosslinking components the total content of Si—H bonds is determined mainly by the octamethylcyclotetrasiloxane to H-polysiloxane ratio whereas the mean molecular weight is determined chiefly by the content of hexamethyldisiloxane as a terminating agent of 2B and 3B (Table II). In this procedure the Si—H bonds withstand well the presence of a strong cation at temperatures about 100°C which permits good equilibration of the prepared polymers.

Influence of Proportion of Vinyl and Si—H Groups on the Sol Content and Crosslink Density

It is obvious that the properties of the vulcanizate are determined by the molecular weights of the vinyl and crosslinking components primarily by the molar ratio of the reactive centres. Therefore, the influence of the vinyl to Si—H molar ratio on the content of extractable substances and crosslink density using components of high (3A + 5B), medium (2A + 4B) and low (1A + 2B) molecular weights was studied. So as not to distort the results by a noncatalyzed

reaction of the Si—H bonds high-temperature post-vulcanization was not performed in this case.

Figure 1 shows the dependence of the sol content in the vulcanizates on the Si—H to vinyl molar ratio. In all cases it was found that the lowest concentration of extractable component, indicating to a certain extent the highest degree of crosslinking, originates when the ratio of Si—H groups to vinyl groups is in the range of 2–5. Also the apparent molecular weight of a network chain M_c is the least at the cited ratios (Fig. 2).

It is of interest that the dependence of both sol content (Fig. 1) and M_c (Fig. 2) on the ratio of reactive groups is more pronounced in the case of low-molecular components (1A + 2B) than in the case of high-molecular ones (3A + 5B). This might be accounted for by the fact that longer chains have a greater probability of steric hindrances thereby suppressing to a certain extent the hydrosilation formation of crosslinks. This could also be responsible for the relatively low content of sol when the ratio of Si—H groups to vinyl ones is higher than 7; a similar explanation has been suggested also by Dontsov.³

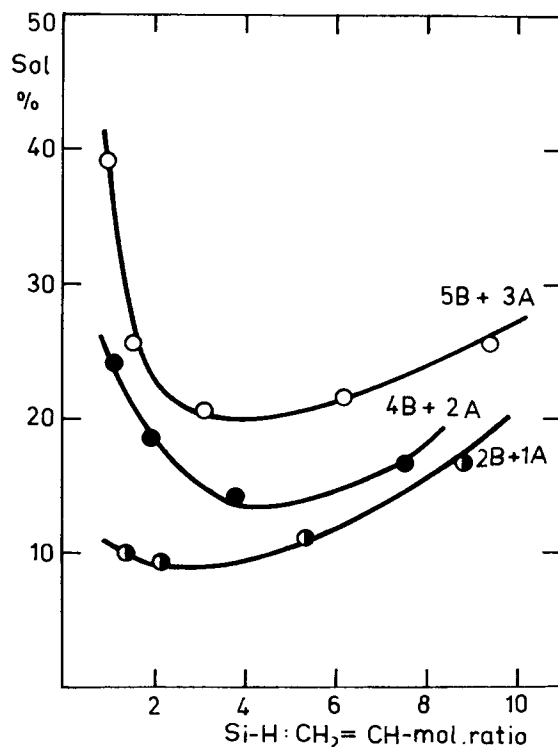


Figure 1 Dependence of sol content on the Si—H to vinyl mol. ratio (for conditions see Experimental).

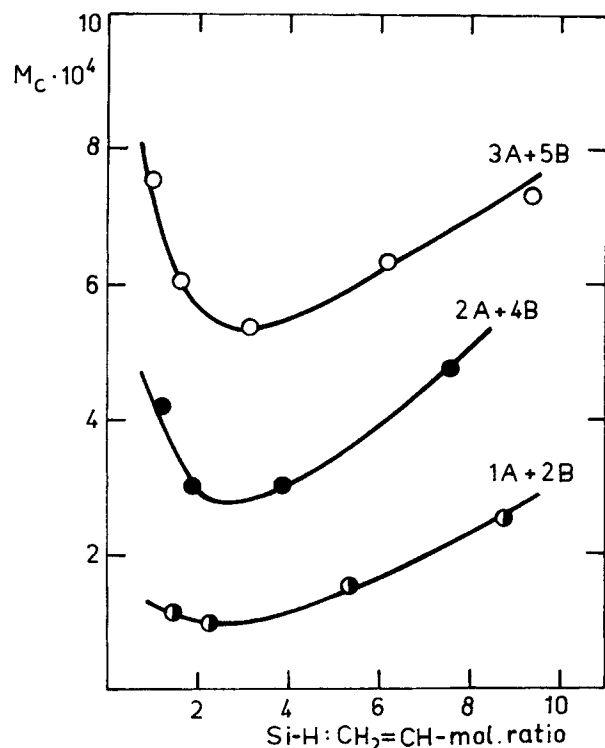


Figure 2 Dependence of apparent molecular weight of network chain of the Si—H to vinyl mol. ratio (for conditions see Experimental).

Influence of Molar Weight of Components on Sol Content and Vulcanizate Crosslink Density

The influence of molar weight of the unsaturated and crosslinking components on the sol content and the crosslink density of vulcanizate was therefore further studied at the optimum ratio of Si—H groups to vinyl groups, 3.5 : 1.

In view of the fact that our goal was to study the hydrosilylation crosslinking of polymers, again postvulcanization was not performed in order to

prevent subsequent noncatalytic reactions of Si—H bonds (Table III). A part of the samples was subjected to postvulcanization, however, which resulted only in a low and proportional decrease in the sol content and a small decrease in the weight of network chains.

These results (Table III) demonstrate a clear dependence of the studied factors on the molecular weights on both components. The sol content at the given mol. weight of vinyl polymer A is only slightly influenced by both the molecular weight and the concentration of Si—H groups in polymer B. On the other hand, when one type of polymer B is used, the effect of molecular weight of polymer A on the amount of the extractable fraction is more pronounced. A similar situation was found in the case of the effect of molecular weights of components A and B on the apparent molecular weight of network chains, M_c . However, at a high molecular weight of the telechelic unsaturated component (3A), undesirably high values of both sol content and M_c are obtained.

For comparison, vulcanization of mixtures 1B to 5B and a nontelechelic unsaturated component 4A containing reactive groups in the polymer chain was carried out. In all these five cases, the values found for M_c and sol content were so high as to be practically unmeasurable. It is evident that in order to obtain a vulcanizate of good quality, a prerequisite is that at least one component of the vulcanization mixture should be telechelic.

Influence of Molar Weight of Components on Mechanical Properties of the Vulcanizate

As for practical applications of silicone vulcanizates their mechanical properties are of primary importance. We studied how these are affected by the molar weights of the components. Again we used a

Table III Influence of Molecular Weight of Vinyl and Crosslinking Polymers on the Content of Extractable Fraction and Apparent Molecular Weight of the Network Chain (M_c)^a

Component B Molecular Weight (Active H, %)	Sol (%), Molecular Weight of Component A			$10^3 \times M_c$ (mol cm ⁻¹), Molecular Weight of Component A		
	34,000	57,000	79,900	34,000	57,000	79,900
2800 (0.365)	7	10	16	6.4	18	38
6000 (0.189)	9	10	20	10	17	58
31,700 (0.181)	8	9	20	8.5	13	27
32,900 (0.085)	10	14	20	13.5	28.5	53
47,800 (0.050)	10	14	22	13	30	60

^a Vulcanization temperature 150°C, Si—H : vinyl groups molar ratio = 3.5 : 1.

Table IV Influence of Molecular Weight of Vinyl and the Crosslinking Polymers on the Mechanical Properties of Vulcanizate^a

Component B Molecular Weight (Active H, %)	Tensile Strength (MPa), Molecular Weight of Component A			Elongation, Molecular Weight of Component A			Hardness, Sh A, Molecular Weight of Component A		
	34,000	57,100	79,900	34,000	57,100	79,900	34,000	57,100	79,900
2800 (0.365)	0.52	0.45	0.18	180	250	330	28	24	12
6000 (0.184)	0.61	0.34	0.25	120	240	360	23	22	12
31,700 (0.181)	0.43	0.49	0.29	120	240	320	20	24	18
32,900 (0.085)	0.37	0.47	0.32	120	240	270	20	20	12
47,800 (0.050)	0.26	0.26	0.23	120	230	230	20	20	12

^a Vulcanization temperature 150°C, then postvulcanization at 200°C; molar ratio Si—H : vinyl groups = 3.5 : 1.

3.5 : 1 ratio of Si—H groups to vinyl groups. In this case, the samples were subjected to postvulcanization prior to measurement, as is usual in practice. When evaluating the data listed in Table IV, it should be mentioned that the mixtures are model ones that contain neither a filler nor a branched unsaturated component, which significantly, positively influences the properties of hydrosilylation¹²⁻¹⁴ silicone rubbers.

Contrary to expectation,¹⁵ the tensile strength of the vulcanizates is pronouncedly decreased with increasing molecular weight of vinyl polymer A. This is evident particularly in the case of polymer 3A. The vulcanizates mostly exhibit low strengths regardless of the crosslinking component B used. Here is an evident connection with the data presented in Table III. The vulcanizates prepared from polymer 3A also exhibited a disproportionately large sol content as well as M_c value. When using an unsaturated polymer with too long a chain, entanglements are likely formed. This retards the hydrosilylation reaction or competes with it. Higher tensile strength of the vulcanizates can therefore be expected in the region of lower and intermediate molecular weights of the unsaturated polymer (approximately in the region of 25,000 to 40,000).

As far as the influence of molar weight of the crosslinking component is concerned, to achieve sufficient mechanical properties, mainly tensile strength, its molar weight should not be too high. For example, in the case of polymer 5B of molecular weight almost 50,000, the attained tensile strengths of the vulcanizate are also low, regardless of the telechelic vinyl polymer used. Therefore, the molecular weight of the crosslinking component should not exceed 30,000. On the contrary, the data presented in Table IV indicate that the rubbers of highest strength could be achieved by crosslinking a vinyl polymer of molecular weight 31,000 with H-polysi-

loxane of molecular weight 6,000. Further improvement of mechanical properties may be expected as a result of addition of branched components, the effect of which is being studied in our laboratory.

REFERENCES

1. K. A. Andrianov, A. V. Gorshkov, A. V. Kruglikov, A. A. Dontsov, V. M. Kopylov, and M. I. Shkolnikov, *Vysokomol. Soed.*, **A21**, 1248-1254 (1979).
2. E. M. Valles and Ch. W. Macosco, *Macromolecules*, **12**, 673, Jul.-Aug., (1979).
3. A. A. Dontsov, Ju. A. Goldovskij, and A. M. Podoba, Structure and properties of nonperoxide cured silicone rubber—Conference internationale du Caoutchouc, 2-4 June 1982, Paris, I-6.
4. F. O. Stark, J. R. Falender, and A. P. Wright, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, and E. W. Adel, Eds., Pergamon, Oxford, 1981, Vol. 2, Chap. 9.3.
5. B. Arkles, *Chem. Technol.*, **542**, (1983).
6. M. Heidingsfeldová and M. Čapka, *J. Appl. Polym. Sci.*, **30**, 1837 (1985).
7. M. Čapka, M. Czakoová, A. Svobodová, and J. Vilím, Int. Cong. Polymers in Electrotechnol., Znojmo, October 1987, p. 31.
8. M. Čapka, M. Heidingsfeldová, J. Hetflejš, and M. Schätz, Czech. pat. 226 278.
9. R. Cramer, *Inorg. Chem.*, **1**, 722 (1980).
10. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1980).
11. M. Čapka, Report 50/85 of Inst. Chem. Process Fundamentals, Czech. Acad. Sci., Prague 1985.
12. Brit. pat. 1 090 958 General Electric Co.
13. GP 1 283 529, K. Seyfried, K. Damm, W. Noll.
14. USP 3 516 946, F. Modic.
15. R. B. Seymour, *Introduction to Polymer Chemistry*, McGraw-Hill, New York, 1971.

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