

Rhodium Complexes as Catalysts for Hydrosilylation Crosslinking of Silicone Rubber

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Synopsis

Vulcanization of silicon rubber compound based on polysiloxanes containing vinyl and Si-H groups catalyzed by $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$, $[\text{RhCl}(1,5\text{-COD})]_2$, $[\text{RhCl}(\text{NBD})]_2$, $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$, and $\text{Rh}(\text{acac})_3$ (1,5-COD = 1,5-cyklooktadiene, NBD = norbornadiene, acac = acetylacetonate) has been studied in dependence on the catalyst, solvent, and reaction conditions. The course of vulcanization as well as the crosslinking density of the vulcanizate and the content of sol indicate that the above catalysts are comparable to and in some cases even better than the widely used hexachloroplatinic acid.

INTRODUCTION

Hydrosilylation crosslinking of silicone rubber is now being increasingly used in rubber manufacture since it has many technological and economical advantages.¹⁻³ Basic components of these silicone rubber compounds are polymethylvinylsiloxanes as a main rubber component and polyhydrogenosiloxanes as a crosslinking component. Even nonfilled, these vulcanizates exhibit very good mechanical properties that are comparable, e.g., to filled radical vulcanizates.⁴

The course of crosslinking and the quality of the vulcanizate depend not only on its composition and the proportion of both polysiloxane components but also on the hydrosilylation catalyst used. However, this problem has so far attracted only little attention. In most applications the classical homogeneous catalyst—hexachloroplatinic acid—has been used, although patent literature claims also other platinum complexes as catalysts for hydrosilylation vulcanization.⁵⁻⁹ These compounds have not been, however, widely exploited.

In recent years, rhodium(I) complexes have been shown to be efficient catalysts for hydrosilylation of olefins by monomeric silicon hydrides.¹⁰ This has led also to their application in hydrosilylation of vinylmethylcyclosiloxanes¹¹ and polymethylvinylsiloxanes,^{12,13} indicating that these complexes could compete with hexachloroplatinic acid even in the vulcanization of silicone rubber. Therefore, it seems useful to study the application of rhodium(I) complexes in more detail, especially as far as the dependence on the structure of catalyst, the type of solvent, and reaction conditions are concerned.

EXPERIMENTAL

Materials

For testing purposes, an experimental noncatalyzed silicone rubber compound corresponding to Rhodorsil RTV 141 kindly provided by Rhone-Poulenc has been used.

Solvents were commercial samples (Lachema, Brno) of chemical purity grade and were used without further purification. The catalysts were prepared by reported procedures, as indicated: di- μ , μ' -chloro-tetra-carbonyldirrhodium¹⁴ {[RhCl(CO)₂]₂}; di- μ , μ' -chloro-tetraethylendirrhodium¹⁵ {[RhCl(C₂H₄)₂]₂}; di- μ , μ' -chloro-di(1,5-cyclooctadiene)dirrhodium¹⁶ {[RhCl(1,5-COD)]₂}; di- μ , μ' -chloro-di(norbornadiene)dirrhodium¹⁷ {[RhCl(NBD)]₂}; chlorotris(triphenylphosphino)rhodium¹⁸ {RhCl[P(C₆H₅)₃]₃}; rhodium(III) 2,4-pentanedionate¹⁹ [Rh(acac)₃]; and (1,5-cyclooctadiene) rhodium 2,4-pentanedionate²⁰ [Rh(1,5-COD)(acac)]. Di- μ , μ' -chloro-tetracyclooctane-dirrhodium supported on Aerosil was prepared so that 10 mg of the rhodium complex dissolved in 100 mL of toluene was added to 10 g of Aerosil 200 or Aerosil R 972 (Degussa); the mixture was freed of the solvent on a rotatory vacuum evaporator and then dried in high vacuo.

Preparation of Vulcanizates and Their Evaluation

The catalysts (as $6.7 \times 10^{-3}M$ solutions) were introduced into the rubber compound manually; the catalyst supported on Aerosil was applied with the aid of a laboratory three roll mill. In all the experiments the catalyst concn was 7 $\mu\text{g/g}$ silicone composition. After the above homogenization, the mixtures tested were cured at 150°C in a hot-air circulation drying oven and the samples were removed at fixed time intervals, to follow the degree of crosslinking. The vulcanizates were evaluated based on equilibrium swelling in toluene (72 h at ambient temperature). Differences in the mass of vulcanizates before swelling, in swelled state, and after drying were used to calculate the procentual content of sol and the network density. The sol characterizes the amount of soluble fractions in the rubber network and the network density expresses the number of crossbonds per volume unit of the vulcanizate. Crosslinking densities were calculated according to the Flory-Rehner equation²¹ [interaction parameter $x = 0.465$ (Ref. 22)].

RESULTS AND DISCUSSION

With respect to the fact that the rate of vulcanization and the quality of the vulcanizate are affected also by the composition of the rubber compound and that the results obtained in hydrosilylation of monomers are scarcely transferable to the reactivity of polymer compounds, we have used in this study only one silicone rubber compound corresponding to the commercial products.

Solvent effects are general feature of the reactions of organometallic compounds²³ and were observed also in hydrosilylation of alkenes²⁴ and phenylalkenes.²⁵ Therefore, the effect of solvents cannot be disregarded also in hydrosilylation crosslinking of polysiloxane chains. For that reason we

have examined this effect with the use of the catalyst, the hydrosilylation activity of which was proved in the case of both monomer¹¹ and polymer¹² substrates.

Results presented in Table I show that the effect of solvents demonstrates not only in the network density achieved but also in the rate of formation of rubber network. Of the solvents used, chloroform is the best one. Its use made it possible to achieve the crosslink density (ν) 0.74 kmol/m³ after 60 min at 150°C or 0.64 kmol/m³ after 30 min at 150°C. Comparison of $\nu = 0.51$ kmol/m³ obtained with chloroform solution after 10-min vulcanization with the corresponding crosslink densities obtained with other solvents shows that also the rate of formation of rubber network and that of establishment of equilibrium state were also fastest with this solvent. After 30–60-min vulcanization, di-*n*-butylether, glycol acetate, and tetrachloromethane solutions behave similarly to the chloroform solution. On the other hand, the lowest crosslinking efficiency was found for the toluene solution. Except for 10-min vulcanization, all the solvents listed in Table I affected the content of sol in the vulcanizates in a similar way.

Observed difference in the effect of solvents can be ascribed either to the change in the catalyst activity or to the change in the mobility of polysiloxane chains or their segments. As only a very small amount of solvent is in fact added to the rubber compound (ca. 0.01 mL/g mixture), the latter possibility is unlikely. Observed changes cannot be, however, related to either dielectric constants of the solvents used or some parameters that characterize their coordinating ability.²³

We believe that significant increase in the activity of the rhodium catalyst in the presence of chloroform could be explained by the cleavage connected with the coordination of the solvent to rhodium. Such a reaction of chloroform with transition metal complexes to give the chloro and dichloromethyl ligand (1) was reported for platinum,²⁶ palladium,²⁷ and ruthenium²⁸ complexes and cannot be thus excluded also in the case of rhodium complexes, as the interaction of silylrhodium complexes with chloromethanes was already reported²⁹:



Therefore, it was of interest to examine whether chloroform increases also the activity of other rhodium catalysts. It was found that vulcanization in the presence of the carbonyl, olefine, or Wilkinson catalyst dissolved in chloroform gives the highest network density (Fig. 1). Already after 10-min vulcanization at 150°C, the crosslinking reaction was so fast that the crosslinking density, e.g., in the case of $[RhCl(CO)_2]_2$ and $[RhCl(1,5-COD)_2]$ was two times higher than with their toluene solutions. The effect of solvent on the catalytic activity is especially marked with the ethylene complexes [see Fig. 1 (e)]. After 10-min vulcanization, acetone, toluene, and dimethylformamide solutions of the above complex did not give gel formation (Table II).

Vulcanization curves shown in Figure 1 illustrate also the effect of the above solvents on the establishment of equilibrium state of crosslinking reactions. From time dependences it becomes clear that in all the cases

TABLE I
Effect of Solvent on Content of Sol and Crosslink Density of Rubber (ν) Obtained by Vulcanization Catalyzed with Rhodium(III) 2,4-Pentanedionate at 150°C

Solvent	10-min vulcanization		30-min vulcanization		60-min vulcanization	
	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)
2-Phenyl-1-propanol	7.5	0.248	4.7	0.400	4.2	0.577
Toluene	8.2	0.252	4.6	0.372	4.2	0.582
2-Propanol	7.1	0.293	4.7	0.434	4.2	0.627
Tetrahydrofuran	5.9	0.315	4.4	0.434	4.1	0.627
Dimethylformamide	8.3	0.330	4.5	0.494	4.1	0.641
Methylethylketone	9.5	0.292	4.5	0.425	4.1	0.615
Dioxane	4.6	0.324	4.3	0.487	4.2	0.632
Pyridine	—	—	4.5	0.488	—	—
Di- <i>n</i> -butylether	6.7	0.352	4.5	0.526	4.0	0.675
1,2-Dimethoxyethane	9.6	0.263	4.9	0.402	4.2	0.564
Chloroform	4.6	0.515	4.3	0.638	3.9	0.736
Tetrachloromethane	4.9	0.338	4.6	0.497	4.1	0.652

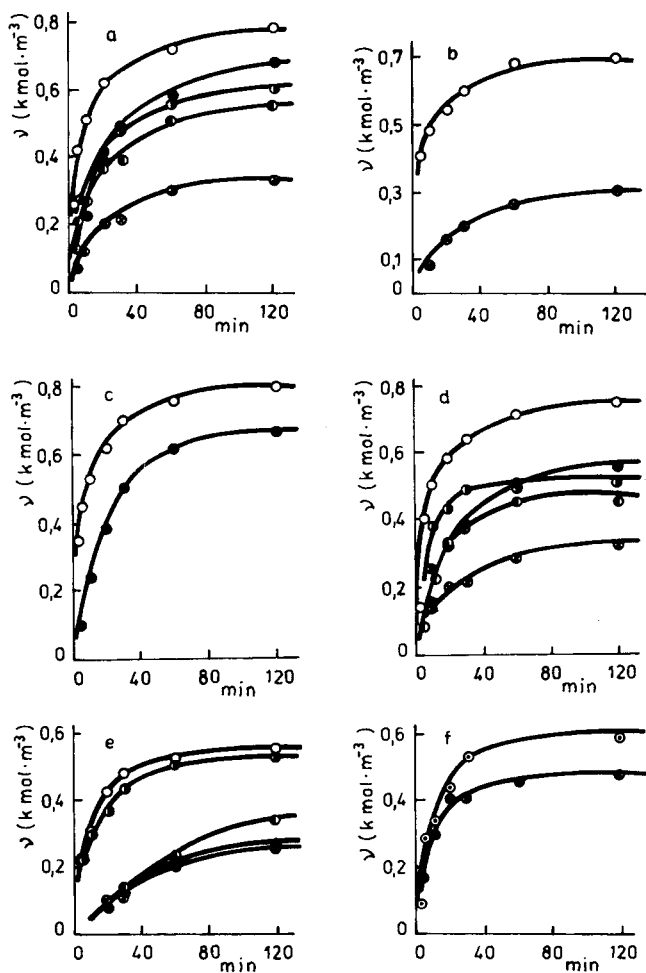


Fig. 1. Vulcanization curves for silicone rubbers in dependence on catalyst and solvent: (a) $[\text{RhCl}(\text{CO})_2]_2$; (b) $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$; (c) $[\text{RhCl}(1,5\text{-COD})]_2$; (d) $[\text{RhCl}(\text{NBD})]_2$; (e) $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$; (f) $[\text{RhCl}(\text{C}_6\text{H}_{14})_2]_2$; supported on Aerosil R 972 (○) and on Aerosil 200 (◐). Solvents: (○) chloroform; (●) toluene; (◐) 2-ethylhexanol; (◑) acetone; (⊗) dimethylformamide.

studied, there is no change in the slope of separate curves. In order to avoid the effect of solvents as co-agents, we have prepared a heterogeneous catalytic system, $[\text{RhCl}(1,5\text{-COD})]_2$ supported on Aerosil 200 or on Aerosil R 972. This catalyst was added to the reaction mixture at the same rhodium concentration as in the foregoing cases. Experimental data show that the catalyst prepared from Aerosil 200 exhibits lesser activity in vulcanization than a similar system prepared from Aerosil R 972 [see Table II, Table III and Fig. 1 (f)]. The difference between both supports is in that Aerosil 200 possesses free surface OH groups while Aerosil R 972 with the comparable specific surface area has these OH groups removed by surface treatment.

The decreased activity of the catalyst on Aerosil 200 is obviously due to a great number of strongly acidic centers that are present on the surface of treated Aerosil R 972³⁰ and which interact likely with the Si—H bonds of the crosslinking agent.

TABLE II
Effect of Solvent and Rhodium Catalyst on Content of Sol and Crosslink Density (ν) of Rubber Obtained by Vulcanization at 150°C

Complex/solvent	10-min vulcanization		30-min vulcanization		60-min vulcanization	
	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)
[RhCl(CO) ₂] ₂						
Chloroform	4.5	0.513	4.1	0.547	3.8	0.718
Toluene	5.2	0.236	4.2	0.487	3.9	0.584
2-Ethylhexanol	4.9	0.331	4.4	0.480	4.1	0.558
Acetone	5.7	0.274	4.8	0.383	4.5	0.518
Dimethylformamide	11.0	0.121	6.1	0.218	5.3	0.309
[RhCl(1,5-COD)] ₂						
Chloroform	4.4	0.530	4.0	0.701	3.9	0.760
Toluene	5.2	0.239	4.2	0.503	3.9	0.624
RhCl[P(C ₆ H ₅) ₃] ₃						
Chloroform	4.4	0.489	4.1	0.605	4.0	0.686
Dimethylformamide	10.0	0.098	7.6	0.269	5.8	0.311
[RhCl(NBD)] ₂						
Chloroform	5.1	0.502	4.5	0.638	4.2	0.720
Acetone	6.1	0.266	4.9	0.389	4.8	0.456
2-Ethylhexanol	5.8	0.379	5.4	0.492	5.1	0.503
Toluene	7.7	0.149	4.9	0.382	4.6	0.511
Dimethylformamide	12.3	0.136	4.9	0.204	5.4	0.281
[RhCl(C ₂ H ₄) ₂] ₂						
Chloroform	7.1	0.307	5.1	0.484	4.7	0.529
Acetone	No vulcanization		17.4	0.118	10.7	0.232
2-Ethylhexanol	6.3	0.318	5.7	0.430	5.7	0.433
Toluene	No vulcanization		10.6	0.121	7.7	0.211
Dimethylformamide	No vulcanization		10.2	0.130	6.7	0.208

TABLE III
Content of Sol and Crosslink Density (ν) of Vulcanizates Obtained with the Use of $[\text{RhCl}(1,5\text{-COD})]_2$ Supported on Aerosil 200 and on Aerosil R 972 (Vulcanization Temperature 150°C)

Vulcanization time (min)	Aerosil R 972		Aerosil 200	
	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)
2	11.2	0.085	—	—
5	6.0	0.290	5.5	0.173
13	5.6	0.341	4.8	0.410
20	5.1	0.438	4.8	0.410
30	4.7	0.537	4.8	0.414
60	4.6	—	4.6	0.450
120	4.5	0.590	4.5	0.478

Let us consider now the activity of dichloro-tetracyclooctadienirrhodium supported on a relatively inert support, Aerosil R 972, in comparison with the activity of dissolved rhodium(I) complexes. From Figure 1 it becomes evident that the complex exhibit similar catalytic properties as $[\text{RhCl}(1,5\text{-COD})]_2$ in toluene, $[\text{RhCl}(\text{CO})_2]_2$ in 2-ethylhexanol, toluene, or acetone, and as $[\text{RhCl}(\text{NBD})]_2$ in toluene, while the activity of these complexes dissolved in chloroform is significantly higher.

If the system $[\text{RhCl}(1,5\text{-COD})]_2$ -Aerosil R 972 is taken as a standard, the efficiency of which is not affected by the solvent, then the above results support the hypothesis about specific activation of the rhodium catalysts by chloroform. On the other hand, strongly polar dimethylformamide is quite unsuitable solvent.

Comparison of the activity of chloroform solutions of the catalysts independence on their structure is also of interest. One has to disregard in this connection the little active dichloro-tetraethylenedirrhodium, both due

TABLE IV
Effect of Catalyst Prepared *in Situ* from Rhodium Complexes and Vinylsilanes on Content of Sol and Crosslink Density of Vulcanizates^a

Rhodium complex	Vinylsilane	Rh:vinylsilane mol. ratio	Sol (%)	Crosslink Density (kmol · m ⁻³)
$[\text{RhCl}(1,5\text{-COD})]_2$	Tetravinylsilane	1:1	4.4	0.763
		1:2	4.6	0.756
	Hexavinylsiloxane	1:1	4.5	0.735
		1:2	4.4	0.735
	Tetramethyltetra- vinylcyclotetrasilox- ane	1:1	4.5	0.749
		1:2	4.6	0.756
Rh(acac)(1,5-COD)	Tetravinylsilane	1:1	4.4	0.726
		1:2	4.2	0.689
		—	4.3	0.758

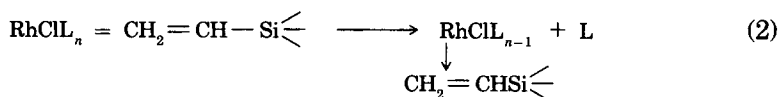
^a Solvent, chloroform; vulcanization temperature, 150°C; vulcanization time, 30 min.

TABLE V
Effect of Solvent and of Sol Content on Crosslink Density (ν) of Vulcanizates Obtained with Hexachloroplatinic Acid at 150°C^a

Vulcanization time(min)	2-Propanol		2-Ethylhexanol		Chloroform	
	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)	Sol (%)	ν (kmol · m ⁻³)
5	11.5	0.110	—	—	—	—
10	4.2	0.436	5.3	0.354	5.7	0.199
20	4.0	0.663	4.0	0.561	4.3	0.396
30	4.0	0.746	4.0	0.623	4.1	0.326
60	3.9	0.829	3.9	0.791	3.8	0.502

^a Pt concn. 14 ppm.

to its relatively low solubility and to its easy decomposition to ethylene and metallic rhodium. According to the crosslinking densities achieved, the other rhodium(I) complexes are very good catalysts differing only little in their activity that, in dependence on ligand, decreases in the sequence: cyclooctadiene > norbornadiene \approx \approx carbonyl > triphenylphosphine. This is in accordance with the assumption³¹ about displacement of these ligands in the coordination sphere of the metal during catalytic hydrosilylation by the vinylsilane group (2), which group then participates in the proper catalytic process:



In view of the fact that some platinum complexes with vinylsiloxane ligands were found to be efficient catalysts,^{7,9} we have paid attention also to similar rhodium complexes. These were prepared *in situ* by the reaction of rhodium complexes with the corresponding vinylsilanes or vinylsiloxanes. As demonstrated by the results summarized in Table IV, the activity of such complexes is the same as that of the catalysts listed in Table II. Furthermore, their activity do not depend either on the structure of the ligand used or on the molar excess of the ligand with respect to the rhodium precursor. Therefore, from the standpoint of application, the use of simple rhodium(I) complexes is more advantageous.

For application purposes, the results obtained with rhodium catalysts were compared with the vulcanization of the same formulation catalyzed by the widely used hexachloroplatinic acid. From the results presented in Table V it is evident that in this case chloroform slows down the reaction compared to the effect of alcohols as solvents. This indicates that here is absent the specific activation of the catalyst by chloroform as in the case of rhodium(I) complexes. When using hexachloroplatinic acid dissolved in isopropanol, we have obtained the same amount of gel and slightly higher crosslinking densities, but on the expense of twice increased metal content in the reaction mixture compared to the rhodium catalysts.

Concluding, we see that rhodium(I) complexes are promising catalysts for hydrosilylation vulcanization of silicone rubber. Their application makes it possible to achieve comparable vulcanization rates and the same quality of the rubber with an smaller amounts of the precious metal than on using traditional catalysts. For that reason they deserve further investigation.

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