

Nonterminal Unsaturated Silane Coupling Agents for Mineral-Filled Ethylene-Propylene Rubber*

PETR VONDRÁČEK, MARTIN ČAPKA, and MIROSLAV SCHÄTZ,
Institute of Chemical Technology, Department of Polymers, 166 28 Prague 6, Czechoslovakia, and Institute of Chemical Process Fundamentals, Czechoslovak Academy of Science, 165 02 Prague 6, Czechoslovakia

Synopsis

This paper describes the results of an experimental investigation concerning the effect of reactive organofunctional unsaturated silanes on mechanical properties of mineral-filled ethylene-propylene elastomers. The tested group of the unsaturated silanes was prepared by hydrosilylation syntheses. The experimental silanes, 2,6-octadienyltriethoxysilane, *cis*-2-butenyltriethoxysilane, 2-(3-cyclohexenylethyl)triethoxysilane, and 2-(3-cyclohexenylethyl)methyldiethoxysilane, led to a considerable improvement in mechanical and electrical properties of mineral-filled vulcanizates based on peroxide-cured ethylene-propylene elastomers. From the tested silanes, the 3-cyclohexenylethylsilanes impart an improvement comparable with the action of vinyltris(2-methoxyethoxy)silane, presently used as a standard coupling agent in mineral-filled peroxide-cured elastomers.

INTRODUCTION

The concept of using organofunctional silanes as coupling agents for mineral-filled rubber is now being widely accepted and employed in rubber technology and manufacture. The silane coupling agents with the appropriate functionality provide chemically bonded coupling between the mineral filler particles and the rubber network. This coupling is apparently responsible for the improved reinforcing action of mineral fillers.

Silane coupling agents are generally organosilicon monomers comprising hydrolyzable alkoxy groups attached to the silicon which react with the surface of the filler, and a reactive organofunctional group (e.g., —SH, —NH₂, —CH=CH₂) bonded via a short alkyl chain to the silicon atom, which reacts with the polymer.

The literature reports numerous processing and physical properties improved by silane coupling agents with white mineral fillers in elastomers.¹⁻⁴ At present, a major area of interest in silane coupling agents for elastomers is in wire and cable applications. The use of the unsaturated silanes, in particular vinyltris(2-methoxyethoxy)silane (Union Carbide Silane A 172) in peroxide-cured white filled poly(ethylene-propylene) elastomers, (EPM, EPDM), greatly increases the modulus and tensile strength and prevents the deterioration of the electrical properties under conditions of high humidity and maintains the electrical properties under actual use.^{3,5,6}

The vinylsilane A 172 has become an industrial standard for EPM and EPDM wire and cable formulations because of its overall cost/performance properties,

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although there are other organofunctional silanes that provide somewhat higher absolute physical property improvements in the system, such as methacryloxypropyltrimethoxysilane (Union Carbide Silane A 174).³ The relative reactivity of the organofunctional group plays a major role in obtaining the optimum performance properties in a mineral-filled peroxide-cured EPDM compound.^{1,2} Consequently, the organofunctionality of the silane is a critical factor, related to the cure mechanism.

It was thought worthwhile to study the effect of silanes containing a relatively more reactive double bond moiety than vinylsilane on the mineral-filled elastomers.⁷ The study of hydrosilylation in the Institute of Chemical Process Fundamentals of the Czechoslovak Academy of Sciences provided a possibility of obtaining the experimental organofunctional silanes with various unsaturated functional groups. This study involves a comprehensive evaluation of the effect of experimental silanes in the peroxide-cured EP elastomers using A 172 silane as a standard.

All the experimental unsaturated silanes tested were prepared by relatively simple syntheses based on hydrosilylation reactions catalyzed by metal complexes, in contrast to the synthesis leading to conventionally used vinylsilane.

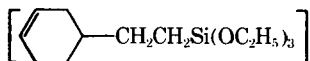
EXPERIMENTAL

Preparation of Silanes

***cis*-2-Butenyltriethoxysilane (BTS)** [$\text{CH}_3\text{CH}=\text{CHCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$]. The silane is a product of the esterification of *cis*-2-butenyltrichlorosilane by ethanol in the presence of an HCl acceptor. The intermediate is obtained by a very rapid reaction of trichlorosilane and 1,3-butadiene. The most suitable catalysts for the addition are palladium(II) complex compounds in a concentration lower than 1.10^{-5} mole per mole of the product.^{8,9} It is also possible to use the nickel complexes¹⁰ as catalysts.

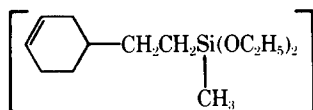
2,6-Octadienyltriethoxysilane (OTS) [$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$]. This silane is prepared by the reaction of triethoxysilane with 1,3-butadiene. The reaction is catalyzed by nickel, cobalt, or palladium compounds. When catalyzed by Pd(II) complexes, the reaction proceeds readily at room temperature with a yield up to 85%. The pure product is very simply separated by distillation.^{8,11} Both the BTS and OTS silanes can be prepared by the hydrosilylation of 1,3 butadiene directly in the raw pyrolytic C₄ fraction.¹¹

2-(3-Cyclohexenylethyl)triethoxysilane (CHTS). This unsaturated silane



can be prepared by hydrosilylation of 4-vinylcyclohexene by triethoxysilane or by hydrosilylation of 4-vinylcyclohexene by trichlorosilane. Both reactions proceed quantitatively with consumption of the chloroplatinic acid of about 2×10^{-5} mole per mole of the product.¹² The starting material for the preparation of the silane, 4-vinylcyclohexene, is a by-product of the cyclodimerization of 1,3-butadiene or the pyrolytic C₄ fraction.

2-(3-Cyclohexenylethyl)methyldiethoxysilane (CHMDS). This silane



is prepared by hydrosilylation of 4-vinylcyclohexene by methyldichlorosilane in the same way as the CHTS silane.¹² All the experimental silanes prepared by hydrosilylation are high-boiling liquids, with boiling points higher than 200°C.

Vinyltris(2-methoxyethoxy)silane (A 172) [$\text{CH}_2=\text{CHSi}(\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_3)_3$]. This unsaturated silane was used as an industrial standard coupling agent in the form of the commercial product Silane A 172, provided by Union Carbide Corp. representatives in Vienna. All vinyl functional silanes are industrially prepared exclusively from the vinylchlorosilane which is obtained by two relatively difficult syntheses. First, the industrially employed method—addition of trichlorosilane to acetylene—has a very exothermic course connected with danger of explosion due to local overheating. The second possibility starts from the carcinogenic vinylchloride, which makes its technology difficult.

Compounding and Test Methods

The effect of the unsaturated silanes was studied in silica (ground quartz)-filled EPDM, compounded according to the following test formulation: EPDM (Intolan 340A), 100; ground quartz (Sikron H 500), 100; zinc oxide, 5; paraffinic oil, 10; dicumyl peroxide 40% (Perkadox BC 40), 7.5–17.5; silane, 1–3.

A comparison of the experimental unsaturated silanes with A 172 was also made in the following typical high-voltage cable calcinated clay-filled EPM formulation: EPM (Vistalon 404), 100; calcinated clay (M 100), 100; zinc oxide, 5; red lead oxide, 4; stearic acid, 2; 2-mercaptobenzoimidazole (antioxidant MB), 2; sulfur, 0.3; dicumyl peroxide (Di-Cup 40C), 7; silane, 1.5.

The compounding was accomplished on a 150 × 400 mm open roll mill during 20–25 min. The addition of 50% of the filler was immediately followed by adding the silane coupling agents in the liquid form on the roll mill using conventional compounding techniques.

The EPDM compounds were vulcanized at 160°C for 25 min in a press, and the EPM compounds were steam cured at 170°C for 13 min. All compound properties were determined by standard testing procedures. Where property determinations are not covered by Czechoslovak Standard procedures (CSN), they are specified in the text of this report.

RESULTS AND DISCUSSION

Ground Quartz-Filled Model Formulation

The effectiveness of the experimental silanes was evaluated in quartz-filled EPDM compounds containing 1, 2, or 3 phr of the respective silane. All three experimental unsaturated silanes improve mechanical properties of the silica-

filled peroxide-cured EPDM. This is shown in Figure 1, where some physical properties such as 100% modulus, tensile strength, and elongation are displayed, for the compound containing 1 phr of each of the tested silanes and 5 phr dicumyl peroxide (12.5 phr Perkadox BC 40). Both 100% modulus and tensile strength increased when the silanes were added. A rather small decrease in elongation was observed with all the silanes used.

When arranged according to their increasing coupling effectiveness in the quartz-filled peroxide-cured EPDM, the order of the silanes was $BTS < OTS < CHTS < A\ 172$. Hardness and resilience remained practically unaffected by the unsaturated coupling silanes, as well as the vulcanization characteristics, measured on an oscillating curometer (Vuremo AC-01, Hungary), as shown in Table I, where the complete performance data of the quartz-filled EPDM are presented.

The addition of A 172 silane to the quartz-filled EPDM resulted in a rather dramatic decrease in Mooney viscosity, as noted in Table II. There is no decrease observed with our silanes. In the conventional calcinated clay-filled compound, the difference between A 172 and CHTS silanes in the compound viscosity was not observed, as is shown in Table III.

The 2-methoxyethanol formed by hydrolysis of A 172 may cause a decrease in the quartz-filled compound viscosity, probably because of its higher boiling point (125°C) in comparison with ethanol generated by hydrolysis of triethoxysilanes. Owing to its higher boiling point, the methoxyethanol cannot escape during mixing and storing from the composition. The plasticizing effect of the remaining 2-methoxyethanol cannot be balanced by the minimum reinforcing action of a ground quartz filler having a surface area of about 2 m²/g.

The influence of silane concentration on tensile strength in the quartz-filled EPDM vulcanized by means of 7 phr dicumyl peroxide is shown in Figure 2. The maximum coupling effect of all silanes is found at 1 phr, with overfilling effect at higher silane concentrations. The silanes at a concentration higher than 1 phr may impart the plasticizing effect to the formulation filled with ground quartz, a filler with a very low reinforcing capacity.

Similar results were obtained with modulus measurements in the vulcanizates cured with 5 phr dicumyl peroxide. The best reinforcing action of A 172 in the system tested is again quite evident from Figure 3.

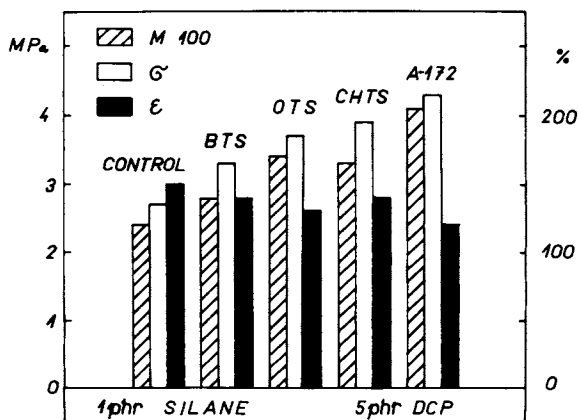


Fig. 1. Mechanical properties of quartz-filled EPDM with various unsaturated silanes.

TABLE I
Evaluation of Unsaturated Silanes in EPDM as Function of Silane and Peroxide Concentration^a

Silane	phr	7.5 phr Dicumyl peroxide 40%						12.5 phr			17.5 phr								
		M 100, MPa	M 200, MPa	TS, MPa	E, %	ShA	R, %	t ₁₀ , min	t ₉₀ , min	M 100, MPa	TS, MPa	E, %	ShA	R, %					
—	0	1.9	2.2	2.3	270	62	54	1.3	16	2.2	2.7	150	65	58	2.6	2.9	110	68	59
BTS	1	1.4	2.5	2.6	225	60	54	1.5	18	3.1	3.3	140	60	54	3.8	3.8	110	68	60
	2	1.6	2.6	3.1	290	55	50	1.3	19	3.0	3.8	160	63	53	3.2	3.4	110	60	60
	3	1.4	2.3	3.1	320	55	52	2.0	19	2.6	4.0	200	60	53	2.6	3.0	120	58	60
OTS	1	1.2	2.7	3.1	260	58	53	2.2	18	3.4	4.2	130	65	58	4.4	4.7	105	70	59
	2	1.7	3.3	3.6	250	57	53	1.4	18	2.8	3.8	140	64	56	3.6	4.0	110	67	62
	3	1.4	2.8	3.8	310	56	50	1.5	18	2.7	4.0	170	64	57	3.1	4.0	140	67	60
CHTS	1	2.5	3.6	3.7	205	58	50	1.8	17	3.3	4.4	140	62	54	—	5.0	90	64	58
	2	2.1	3.4	3.8	270	56	49	1.9	19	2.9	4.0	170	59	53	4.2	4.4	110	60	58
	3	1.5	2.6	3.7	320	56	48	1.7	18	2.6	4.0	190	58	54	3.8	4.4	110	60	58
A 172	1	2.3	—	4.4	165	63	55	1.7	18	4.1	4.8	120	67	60	—	5.5	85	71	64
	2	3.5	—	5.1	150	60	54	1.5	17	5.0	5.1	105	65	60	—	5.1	90	69	62
	3	3.4	—	4.9	140	59	54	1.3	19	4.2	5.5	125	65	53	—	4.5	90	62	63

^a Formulation: EPDM, 100; ground quartz, 100; zinc oxide, 5; paraffinic oil, 10; DCP, 40%, as shown; silane, as shown. M 100, 100% modulus; M 200, 200% modulus; TS, tensile strength; E, elongation at break; R, resilience; Sh A, Shore hardness; t₁₀, Vuremo scorch time; t₉₀, Vuremo optimum cure time.

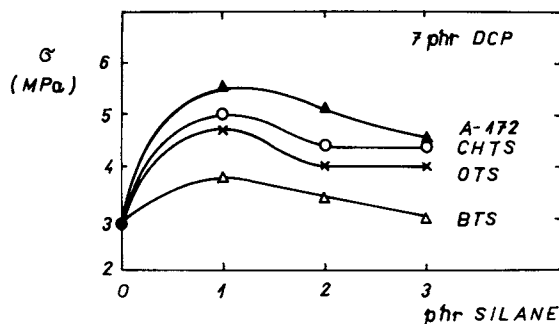


Fig. 2. Tensile strength of quartz-filled EPDM with various concentrations of different unsaturated silanes.

TABLE II
Effect of Silane Coupling Agents on Mooney Viscosity in Quartz-Filled Peroxide-Cured EPDM

Silane (1 phr)	Mooney viscosity ML-4 (100°C)
Control, no silane	15
BTS	15
OTS	14
CHTS	14
A 172	5

TABLE III
Effect of Unsaturated Silanes on Processing Performance in High-Voltage EPM Cable Formulation

	Silane (1.5 phr)		
	CHTS	CHMDS	A 172
Mooney viscosity ML-4			
150°C	40	41	44
170°C	40	45	42
Mooney scorch t_5 , min			
150°C	5	4	3.5
170°C	2.5	2	2
Mooney cure rate, MS/min			
150°C	7.5	8.5	7.5
170°C	20	30	20

The effect of changing peroxide level on the mechanical properties of silica-filled EPDM was also investigated in the concentration range of 3 to 7 phr dicumyl peroxide. From Figure 4 it is obvious that increasing the peroxide level in the quartz-filled EPDM containing the unsaturated silanes results in a considerably higher reinforcing action. The increased peroxide concentration leads to rather substantial improvements in tensile strength when compared with the appropriate controls. The relative order of coupling effectiveness of the silanes remains unchanged by changing the peroxide concentration.

The situation is a little different with the dependence of 100% modulus on the peroxide level, as shown in Figure 5. The 100% modulus was found practically unaffected by addition of the new unsaturated silanes BTS, OTS, and CHTS at low levels of peroxide, while A 172 silane showed a considerable improvement even at the standard level of peroxide. The peroxide content increase resulted

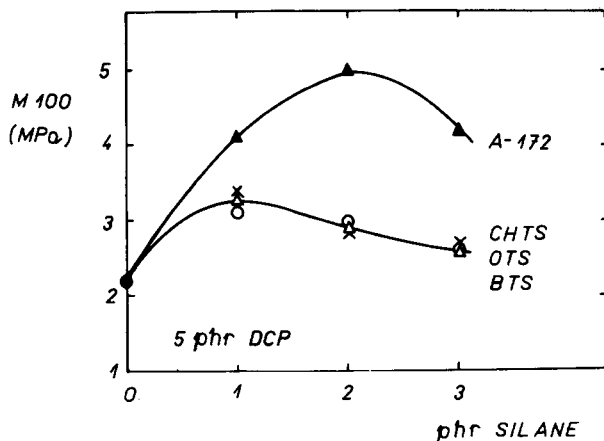


Fig. 3. 100% Modulus of quartz-filled EPDM with various concentrations of different unsaturated silanes.

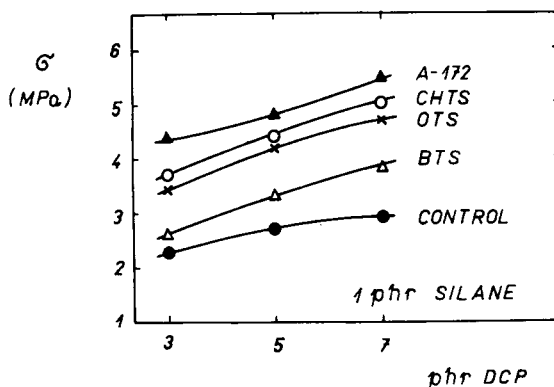


Fig. 4. Tensile strength of quartz-filled EPDM with various unsaturated silanes as a function of peroxide concentration.

in a considerable improvement of elastomer-filler reinforcement, indicated by the modulus enhancement.

Summarizing the first part of our study, we can say that the coupling effectiveness of the group of nonterminal unsaturated silanes obtained by hydrosilylation reactions has been shown in the mineral-filled peroxide-cured EPDM rubber. When compared with the conventional A 172 silane, the effectiveness of CHTS silane is nearly the same, especially in the tensile strength improvement at higher peroxide levels. BTS and OTS silanes do not provide as high a level of the rubber-filler coupling action as A 172 in the model quartz-filled peroxide-cured EPDM formulation.

Calcinated Clay-Filled High-Voltage Cable Formulation

3-Cyclohexenylethyl functional silanes were therefore chosen for testing in the typical high-voltage calcinated clay-filled EPM cable formulation, along with the standard A 172. Two different 3-cyclohexenylethylsilanes with two or three hydrolyzable ethoxy groups in a molecule, viz., CHTS (triethoxysilane) and CHMDS (methyldiethoxysilane), were used in the comparative experiment.

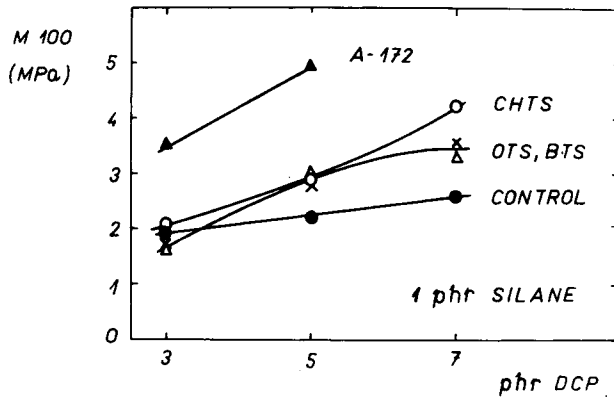


Fig. 5. 100% Modulus of quartz-filled EPDM with various unsaturated silanes as a function of peroxide concentration.

There was no substantial difference among the three tested unsaturated silanes in the high-voltage cable formulation. This is evident from Table III as to the processing and cure performance and from Table IV as to the mechanical properties. In Table IV are also given mechanical properties of vulcanizates heat aged at 130°C for 10 days.

Results of measuring electrical properties of the vulcanizates are given in Table V. Again, no difference was found in the improving action of A 172 vinylsilane and the experimental 3-cyclohexenylethylsilanes. All the silanes were found to be equivalent in their coupling and improving activity in the standard calci-

TABLE IV
Effect of Unsaturated Silanes on Mechanical Properties in High-Voltage EPM Cable Formulation^a

	Silane (1.5 phr)		
	CHTS	CHMDS	A 172
100% Modulus, MPa	1.4 (1.9)	1.2 (1.7)	1.4 (1.7)
300% Modulus, MPa	1.9 (2.7)	1.6 (2.3)	1.9 (2.5)
Tensile strength, MPa	5.3 (5.4)	5.2 (5.4)	5.5 (5.7)
Elongation at break, %	820 (780)	840 (800)	860 (840)
Tensile set at break, %	43 (41)	47 (52)	55 (57)

^a Data in parentheses were obtained with samples heat aged at 130°C for 10 days.

TABLE V
Effect of Unsaturated Silanes on Electrical Properties in High-Voltage EPM Cable Formulation

	Silane (1.5 phr)		
	CHTS	CHMDS	A 172
Specific resistance, ohm-cm	7.2×10^{15}	2.5×10^{15}	6.7×10^{15}
Dissipation factor (800 Hz)	0.0027	0.0029	0.0031
Dielectric constant	2.98	2.90	2.87
Dielectric strength, kV/mm	28.0	28.0	27.2
Immersed in 70°C Water for 7 Days			
Specific resistance, ohm-cm	3.8×10^{15}	6.9×10^{15}	6.9×10^{15}
Dissipation factor (800 Hz)	0.0028	0.0034	0.0031
Dielectric constant	3.00	2.72	2.98
Dielectric strength, kV/mm	28.0	26.5	28.3

nated clay-filled peroxide-cured EPM formulation. The wet electrical properties are protected to the same degree with all the silanes tested.

It was confirmed that two hydrolyzable filler-reactive ethoxy groups are sufficient for ensuring the proper coupling action of the silane to the white filler surface.

CONCLUSIONS

The data obtained in this study indicate a class of unsaturated organofunctional silanes prepared by hydrosilylation that are active as coupling agents in peroxide-cured mineral-filled EPM and EPDM compounds. The coupling activity of this new group of coupling agents, developed in the Institute of Chemical Process Fundamentals of the Czechoslovak Academy of Sciences, was found to be of the same level as that of the now conventionally used A 172 vinylsilane.

The use of both A 172 and the studied unsaturated silanes clearly improves the mineral filler reinforcement in peroxide-cured EP vulcanizates without affecting the cure rate properties over the control. It may be that with those nonterminal unsaturated coupling agents an enhanced utilization of unsaturated silanes in the compound is realized using higher levels of peroxide, such as was already described for A 172 silane.² The improvements afforded by the use of the experimental unsaturated silanes in the high-voltage cable formulation are the same as those of A 172 silane. The coupling activity of the tested group of the unsaturated silanes, along with their relatively simple syntheses, might become a base for their industrial production and application.

Although the economy of production of the studied silanes has not yet been confirmed on an industrial scale, the preliminary estimate of the production cost of 3-cyclohexenylethylsilanes leads to a 20–30% cost decrease in Czechoslovakia when compared with the cost of importing Union Carbide A 172 silane.

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