



SiO₂-FILLED POLYDIMETHYLSILOXANE COMPOSITIONS FUNCTIONALIZED WITH CARBOXY AND THIOETHER GROUPS

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Cite this: *INEOS OPEN*,
2024, 7 (1–3), 69–72
DOI: 10.32931/io2429a

Received 26 April 2024,
Accepted 12 July 2024

<http://ineosopen.org>

Abstract

The possibility of application of carboxy- and thioether-containing alkoxy-silanes as additives in the formation of elastomeric SiO₂-filled polydimethylsiloxane (PDMS) compositions cured with zirconium siloxanes has been studied. It is shown that the introduction of these additives into the system ensures an increase in the dielectric constant, provided that the final components are compatible (up to $\epsilon' \geq 4$ at $f=10^2$ Hz). By varying the composition and initial ratio of the components, it is possible to achieve the desired mechanical characteristics suitable for using the resulting materials as actuators.

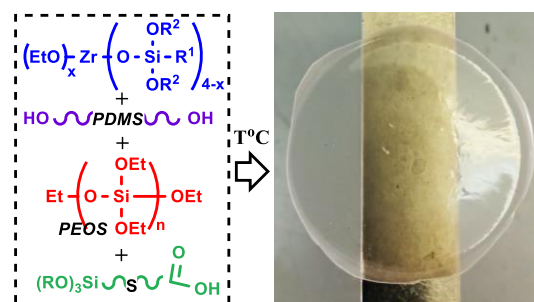
Key words: hydrothiolation, alkoxy-silanes, metallosiloxanes, elastomers, permittivity.

Introduction

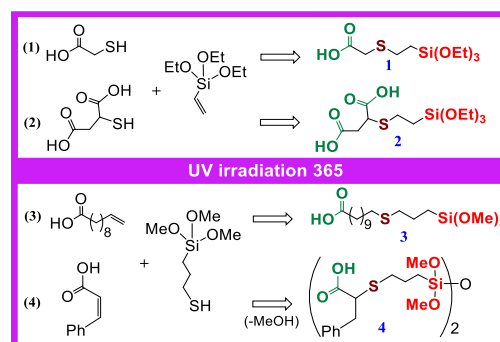
Dielectric elastomers are currently used in engines, optical devices, sensors, energy storage devices, robotics, artificial muscles, *etc.* [1]. Silicones are among the most promising polymers that can be used as dielectric elastomers [2]. One of the methods for increasing the dielectric constant of silicones is the introduction of polar groups of various natures into the chain structure [3, 4]. Earlier we have demonstrated the possibility of production of elastomeric materials filled with a silica component based on PDMS, obtained by curing with functional metallosiloxanes (MSs), which have improved dielectric characteristics in the frequency range of 10⁻¹–10² Hz relative to the industrial silicones [5, 6]. The dielectric constant was affected by both the MS functionality and the presence of the SiO₂ component. Nevertheless, this approach to the formation of elastomeric materials allows their modification by additional introduction of functional alkoxy-silanes, capable of cross-linking with the material network. In this work, the possibility of improving the dielectric characteristics by the additional introduction of carboxy-containing alkoxy-silanes into the system was explored.

Results and discussion

A series of carboxy-containing alkoxy-silanes 1–4 were obtained by the hydrothiolation under UV radiation using functional thiols, alkoxy-silanes, and organic acids (Scheme 1). The characteristic feature of the process was the long reaction time due to the reduced reactivity of the vinyl group in the thiolation (in the case of compounds 1 and 2), steric hindrances (in the case of 2), and the internal nature of the double bond (in the case of 4). According to the results of the ¹H NMR



spectroscopic studies, product 1 contained up to 10% of the α -addition product, while compound 4 was obtained as a disiloxane, which is explained by the prolonged impact of UV radiation on the methoxy groups (Fig. 1) [7].



Scheme 1. Synthesis of compounds 1–4.

By the example of the production of PDMS compositions cured with zirconium siloxane oligomers, the possibility of application of compounds 1–4 as the additives for potential

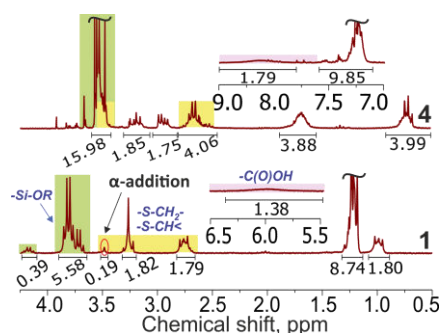


Figure 1. ¹H NMR spectra of compounds 1 and 4.

increase in the dielectric constant of the compositions was investigated, since they contain polar carboxy and thioether groups and are capable of binding to all components of the initial system, thus being incorporated into the formed hybrid network of the material (Fig. 2).

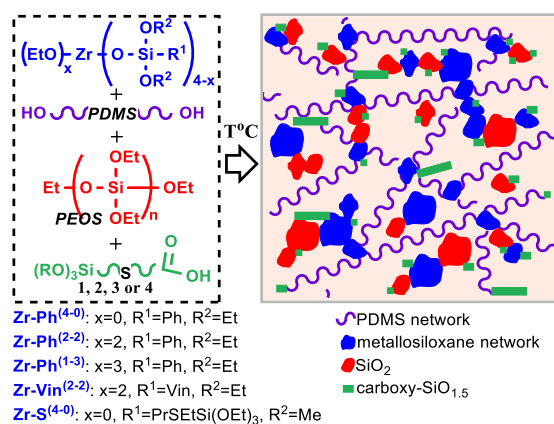


Figure 2. Formation of the material and structures of the zirconium siloxanes in use.

A series of MS/PDMS/polyethoxysiloxane (PEOS)/additive compositions were obtained, and their mechanical and dielectric properties were compared to those previously obtained in the absence of an additive.

Using the most active zirconium siloxane in terms of cross-linking ability **Zr-Ph⁽¹⁻³⁾**, it was shown that the overall compatibility of the components for the systems of initial composition {**Zr-Ph⁽¹⁻³⁾**/SKTN-E/PEOS/additive} decreases in the series **1**→**4**→**3** (Table 1). In the case of compound **3**, this can be explained by the poor molecular compatibility of the undecyl moiety with dimethylsiloxanes. In the case of compound **4**, this can be explained by the shielding effect of the bulky substituent at the silicon atom and the propensity to form its own network, being introduced into the system in a large amount, even despite the presence of a phenyl group providing the affinity to PDMS. Compound **1** is free from these two drawbacks; therefore, it affords uniform compositions in a wider range of ratios of the initial components. Its application allows for a significant increase in the permittivity of the material in the frequency range $f \leq 10^2$ compared to the compositions deprived

of the additives, while some decrease in the elastomeric properties is observed.

Table 2 shows the characteristics of the compositions obtained using an extended series of zirconium siloxanes, PDMSs of different molecular weights, and additives **1**, **2**, and **4**. The general trends regarding the dielectric and mechanical properties are maintained.

Among the key features, of note are the following ones. The compatibility of the components decreases in the series of the additives **1**→**2**→**4** and with an increase in their content. In the case of compound **2**, this can be connected with an increased concentration of carboxy groups. Better compatibility can be achieved by using partially siloxy-substituted zirconium siloxanes as curing agents or PDMS blocked with (3-aminopropyl)triethoxysilane. The choice of rubber affects the kinetics of the network formation, while a decrease in its molecular weight and, therefore, an increase in the functionality of silanol groups allow for an increase in the material uniformity. However, this reduces the dielectric properties but increases the elasticity of the composition, which was observed earlier [8, 9]. A significant increase in the dielectric constant was achieved by using additive **1** and higher molecular weight rubber SKTN-E, which should contribute to the formation of larger domains formed during the condensation of MS, PEOS, and the additive. In some cases, it is possible to increase the dielectric constant to $\epsilon' \geq 4$ even at $f = 10^2$, while maintaining sufficient strength and elasticity of the material. The main factor that affects the dielectric properties is the compatibility of the components of the final system. For illustration, Fig. 3 shows the appearance of selected compositions of different initial formulations and Fig. 4 shows an example of the IR spectrum of the carboxy-containing composition.

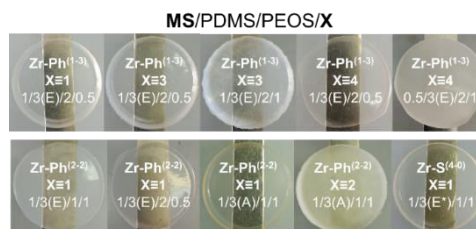


Figure 3. Appearance of the selected compositions of different initial formulations (X is the carboxy-containing additive).

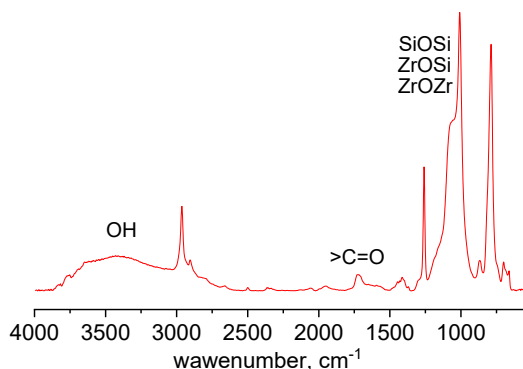
Table 1. Characteristics of the compositions obtained by curing the initial mixtures **Zr-Ph⁽¹⁻³⁾**/SKTN-E/PEOS/X (where X is the carboxy-containing additive)

X	Ratio, wt.pt.	ϵ' ($f = 1/10/100$ Hz)	ϵ''	$\sigma \cdot 10^{11}$, S/cm	$\text{tg } \delta$	$\sigma \pm \Delta\sigma$, MPa	$\epsilon \pm \Delta\epsilon$, %	Characteristic
–	1/3/2/–	4.8/3.6/3.3	2.4/0.6/0.2	0.1/0.3/0.9	0.5/0.2/0.05	8.2±0.2	28±2	
1	1/3/2/0.1	4.6/3.8/3.5	1.8/0.4/0.1	0.1/0.3/0.7	0.4/0.1/0.03	4.9±0.3	4±1	Transparent, homogeneous, yellowish
	1/3/2/0.5	14.6/5.7/4.3	16.6/3.5/0.8	0.9/2.1/18.2	1.1/0.6/0.2	8.1±0.3	11±1	
	0.5/3/2/1	27.7/8.1/5.4	55.9/9.4/2.2	3.2/5.6/10.8	2.0/1.2/0.4	4.2±0.1 ^a	25±11	
	1/3/1/1	15.0/5.8/4.1	17.6/4.0/1.1	1.0/2.4/5.4	1.2/0.7/0.2	4.2±0.1	13±1	
3	1/3/2/0.5	5.1/3.3/2.8	2.8/0.8/0.3	0.2/0.5/1.3	0.6/0.2/0.1	6.5±0.2	8±0.2	Opalescent, colorless
	1/3/2/1	5.3/3.4/3.0	3.4/0.8/0.3	0.2/0.5/1.4	0.6/0.2/0.1	3.6±0.2 ^b	70±24	Heterogeneous, cloudy
4	1/3/2/0.5	5.1/4.0/3.7	1.9/0.5/0.2	0.1/0.3/0.9	0.4/0.1/0.04	8.3±0.1 ^a	28±9	Transparent, homogeneous, yellowish Heterogeneous, white-yellow
	0.5/3/2/1	3.9/3.3/3.2	0.7/0.3/0.1	0.04/0.2/0.5	0.2/0.1/0.02	3.5±0.1	384±24	

a/b—break during the neck formation/spreading; σ is the tensile strength; ϵ is the elongation at break; ϵ' is the dielectric constant; ϵ'' is the dielectric loss; σ' is the conductivity; $\text{tg } \delta$ is dielectric loss tangent.

Table 2. Characteristics of the compositions obtained by curing the initial mixtures MS/SKTN/PEOS/X (where X is the carboxy-containing additive)

MS	X	Ratio, wt.pt.	ε' ($f = 1/10/100$ Hz)	ε''	$\sigma' \cdot 10^{11}$, S/cm	$tg \delta$	$\sigma \pm \Delta\sigma$, MPa	$\varepsilon \pm \Delta\varepsilon$, %	Characteristic
Zr-Ph ⁽⁴⁻⁰⁾	–	1/3(E)/2/–	7.1/4.5/3.8	2.0/1.2/0.3	0.1/0.7/1.7	0.3/0.3/0.1	5.6±0.3	14±2	Transparent, homogeneous, yellowish
	1	1/3(E)/2/0.5	6.9/4.6/3.9	4.4/1.2/0.4	0.3/0.7/1.9	0.6/0.3/0.1	4.1±0.1	251±28	Heterogeneous morphology
		1/3(E)/1/1	–	–	–	–	–	–	–
		1/3(A)/1/1	10.1/5.2/4.0	12.1/2.3/0.6	0.9/2.9/17.7	1.2/0.4/0.2	4.9±0.3	101±23	Transparent, homogeneous, yellowish
	2	1/3(A)/2/0.1	4.3/3.6/3.5	1.3/0.3/0.1	0.2/1.6/14.0	0.3/0.1/0.02	6.2±0.2	144±3	Heterogeneous, cloudy
		1/3(A)/2/0.5	3.7/3.4/3.4	0.6/0.1/0.03	0.2/1.5/13.4	0.2/0.03/0.01	3.1±0.1	55±3	Heterogeneous morphology
	4	1/3(E)/2/0.5	–	–	–	–	–	–	–
	Zr-Ph ⁽²⁻²⁾	–	1/3(E)/2/–	5.8/4.1/3.6	3.7/0.8/0.2	0.2/0.5/1.3	0.6/0.2/0.1	6.5±0.1	35±3
1		1/3(E)/2/0.5	7.5/4.9/4.1	6.0/1.4/0.5	0.3/0.9/2.3	0.8/0.3/0.1	5.1±0.1 ^b	176±35	Opalescent, yellowish
		0.5/3(E)/2/1	13.2/6.8/4.9	25.8/4.3/1.3	1.5/2.6/6.3	2.0/0.6/0.2	3.4±0.1	50±8	Transparent, homogeneous, yellowish
		1/3(E)/1/1	9.0/4.8/3.8	8.9/1.9/0.6	0.5/1.1/3.0	1.0/0.4/0.1	4.1±0.2	170±25	Opalescent, yellowish
2		1/3(A)/1/1	7.4/4.8/4.0	7.9/1.6/0.5	0.6/2.5/16.8	1.1/0.3/0.1	5.5±0.3	115±23	Transparent, homogeneous, yellowish
		1/3(A)/2/0.1	5.4/4.1/3.7	2.7/0.6/0.1	0.3/1.9/15.7	0.5/0.2/0.1	7.8±0.2	128±22	Heterogeneous, cloudy
4		1/3(A)/2/0.5	4.3/3.5/3.4	1.2/0.3/0.1	0.2/1.5/13.5	0.3/0.1/0.02	6.5±0.2	70±2	Heterogeneous, cloudy
		1/3(E)/2/0.5	5.1/3.9/3.6	1.8/0.5/0.2	0.1/0.3/0.9	0.4/0.1/0.04	5.4±0.1 ^b	173±36	Opalescent, yellowish
–		0.5/3(E)/2/1	4.1/3.5/3.3	0.7/0.2/0.1	0.04/0.1/0.4	0.2/0.1/0.02	2.5±0.03	293±15	Heterogeneous, cloudy
Zr-Vin ⁽²⁻²⁾		–	1/3(E)/2/–	6.6/4.4/3.8	5.0/1.1/0.3	0.3/0.7/1.8	0.8/0.3/0.1	6.0±0.1 ^a	33±14
	1	1/3(E)/2/0.5	11.6/5.7/4.5	19.1/3.1/0.9	1.1/1.9/4.3	1.7/0.6/0.2	5.5±0.2 ^b	330±97	Opalescent, yellowish
		1/3(A)/1/1	3.8/3.6/3.6	0.3/0.1/0.03	0.2/1.6/20.5	0.1/0.02/0.01	7.3±0.2	54±5	Opalescent, yellowish
	4	1/3(E)/2/0.5	5.4/4.1/3.8	2.3/0.6/0.2	0.1/0.4/1.0	0.4/0.1/0.05	5.8±0.2 ^a	51±24	Opalescent, yellowish
Zr-S ⁽⁴⁻⁰⁾	–	1/3(E*)/2/–	10.3/6.0/3.7	8.1/2.7/0.9	0.5/1.6/5.2	0.8/0.4/0.2	1.6±0.1	174±29	Transparent, homogeneous, yellowish
	1	1/3(E*)/1/1	13.4/6.9/4.8	22.9/4.3/1.4	1.3/2.6/7.1	1.7/0.6/0.3	2.4±0.1	51±2	Transparent, homogeneous, yellowish

**Figure 4.** IR spectrum of the film surface of initial composition {Zr-Ph⁽²⁻²⁾/SKTN-E/PEOS/1} = 0.5/3/2/1 wt. pt.

Experimental section

Methods and materials

The ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer (Germany) at room temperature using standard pulse sequences of Bruker software. MestRenova software was used for analysis.

The dielectric characteristics were measured using a Novocontrol Alpha-A impedance analyzer (Installation Concept 40) and a ZGS Alpha Active Sample Cell dielectric cell with 20 mm diameter gold disk electrodes (Germany). The measurements were carried out in the frequency range of 10^{–1}–10⁶ Hz at room temperature.

The mechanical properties of the resulting compositions were determined on a Shimadzu Autograph AGS-H universal testing machine (Japan) in the uniaxial tension mode. The samples were tapes with the working part sizes of 3 × 20 mm;

the stretching rate was 10 mm/min. The IR spectra were recorded on a Bruker Tensor 27 spectrometer (Germany)

The experiments were carried out with a UV LED lamp (365 nm, 70 W).

PDMS rubbers of SKNT-A (MW~20000, 1.5–2 Pa·s) and SKTN-E (MW~120000, 80–120 Pa·s) trademarks were used in the work. Mercaptoacetic acid (MA, ABSCR), D,L-mercaptopropionic acid (MSA, 99%, Acros), undecylenic acid (UndA, Acros), cinnamic acid (CinA), and (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%, ABCR) were purchased from commercial sources and used without additional purification. Triethoxy(vinyl)silane (TEVS) was distilled under an argon atmosphere prior to use. Toluene, methanol, and ethanol were dried by prolonged boiling and distillation over CaH₂ under argon and stored over 3Å molecular sieves.

Syntheses

Carboxy-containing alkoxy-silanes **1–4** were obtained by UV irradiation (365 nm) of a mixture of the corresponding thiol and olefin (in solution) at a molar ratio of [HS]:[C=C] = 1:1 under an argon atmosphere. The reaction was monitored by ¹H NMR spectroscopy based on the disappearance of the signals of double bond protons in the region of $\delta_{\text{H}} \sim 5.5$ –6.5 ppm.

Compound **1** was obtained from MSA (13.59 g, 0.1475 mol) and TEVS (28.08 g, 0.1475 mol) in a quantitative yield. The irradiation lasted 18 h. The compound was stored and used in the neat form. ¹H NMR (CDCl₃): δ 0.90–1.11 (m, 1.9H, SiCH₂), 1.14–1.50 (m, 9.1H, –CH₃, CH₂CH<), 1.89–2.13 (m, 0.2H, SiCH<), 2.65–2.85 (m, 1.8H, S-CH₂CH₂), 3.26 and 3.48 (both s, 2H, S-CH₂-C(O)OH), 3.72, 3.81, and 4.17 (q, 6H, OCH₂, $J = 7.1$ Hz), 5.99 (br. s, 1H, –C(O)OH) ppm.

Compound **2** was prepared from a solution of MSA (5.73 g, 0.0381 mol) and TEVS (7.26 g, 0.0381 mol) in ethanol (10 mL) in a quantitative yield. The irradiation lasted 47 h. The compound was stored and used as a solution. ^1H NMR (DMSO- d_6): δ 0.70–1.45 (m, 11H, SiCH₂, –CH₃), 2.54–2.93 (m, 4H, S-CH₂CH₂, CH₂-C(O)OH), 3.37–3.88, 3.98–4.46 (both m, 7H, S-CH₂-C(O)OH, OCH₂), 12.60 (br. s, 2H, –C(O)OH) ppm.

Compound **3** was prepared from a solution of UndA (6.70 g, 0.0364 mol) and MPTMS (7.15 g, 0.0364 mol) in 32 mL of dry methanol in a quantitative yield as a clear, low-viscosity, yellowish liquid. The irradiation lasted 4 h. It was stored and used in the neat form. ^1H NMR (CDCl₃): δ 0.740 (t, 2H, SiCH₂, J = 8.4 Hz), 1.14–1.44, 1.46–1.78 (m, 18H, CH₂), 2.32 (t, 2H, CH₂-C(O)OH, J = 7.5 Hz), 2.49 (q, 4H, SCH₂, J = 7.8 Hz), 3.55 (s, 9H, OCH₃) ppm.

Compound **4** was prepared from a solution of CinA (5.02 g, 0.0339 mol) and MPTMS (6.66 g, 0.0339 mol) in 25 mL of dry methanol in 90% yield relative to the theoretical product as a transparent viscous orange liquid. The irradiation lasted 60 h. The compound was stored and used in the neat form. ^1H NMR (CDCl₃): δ 0.51–0.93 (m, 4H, SiCH₂), 1.44–1.93 (m, 4H, CH₂), 2.45–2.80 (m, 4H, SCH₂), 2.83–3.00, 3.06–3.30 (both m, 4H, PhCH₂), 3.40–3.60 (m, 14H, OCH₂, CH-C(O)OH), 7.03–7.66 (m, 10H, Ph), 8.12 (br. s, 2H, –C(O)OH) ppm.

The synthesis of the zirconium siloxanes in use and the method for producing the compositions are described elsewhere [6, 8, 9].

Conclusions

A series of the carboxy- and thioether-containing alkoxy-silanes were synthesized. The possibility of application of the resulting compounds as the additives during the formation of elastomeric compositions based on PDMS cured with zirconium siloxanes and filled with a silica component was studied. It was shown that the effect of increasing the permittivity when introducing carboxy and thioether functions into the system is determined to a greater extent by the compatibility of the final components of the cured system. In some cases (using compound **1**), it is possible to increase the permittivity of the material $\epsilon' \geq 4$ in the frequency range $f \leq 10^2$. By varying the composition and initial ratio of the components, it is possible to achieve the desired mechanical characteristics suitable for using the resulting materials as actuators. The silanes obtained in this work can also be further used as comonomers for producing siloxane resins.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 19-73-30028).

The NMR and IR spectroscopic studies and the investigation of mechanical properties were performed using the equipment of the collaborative access center "Center for Polymer Research" of ISPM RAS with financial support from the Ministry of Science and Higher Education of Russian Federation (FFSM-2024-0001). The dielectric measurements were carried out using the equipment of the National Research Center Kurchatov Institute.

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