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Electronic Supplementary Information

Similar nature leads to improved properties: cyclic organosilicon triperoxides promising curing agents for liquid polysiloxanes

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I. Monitoring of silicone curing

1.1 Curing times

Table S1. Curing times of PDMS-a, PDMS-b and PDMS-b/PMHS mixture.

Curing agent	T, °C	Concentration		τ_{curing}		
		% wt.	C, mol/L	PDMS-a	PDMS-b	PDMS-b+PMHS
DBP	110	1	0.04	17 h	13 h	7 h
		3	0.15	4 h (foaming)	2 h (foaming)	30 min (foaming)
1	130	7	0.22	–	–	–
	150	1	0.03	–	–	11.5 h
		3	0.09	–	13.5 h	5 h
		5	0.15	–	5 h	2 h
		7	0.22	–	1.5 h	1 h 15 min
	180	1	0.03	–	9.5 h	5.5 h
		3	0.09	–	2 h 45 min	1 h 15 min
		5	0.15	–	1 h 45 min	1 h
		7	0.22	>10 h	1 h	45 min
2	150	3	0.09	–	13.5 h	3.5 h
		5	0.15	–	6 h	2.5 h
		7	0.21	–	2 h	1 h 45 min
	180	1	0.03	–	–	11 h
		3	0.09	–	8 h	2 h 45 min
		5	0.15	–	4.5 h	2 h
		7	0.21	>10 h	1 h 45 min	1.5 h
3	180	1	0.03	–	–	–
		3	0.09	–	–	–
		5	0.15	–	–	24 h
		7	0.21	–	12 h	7 h
4	180	7	0.16	–	–	–
		9	0.20	–	–	–

1.2 IR data

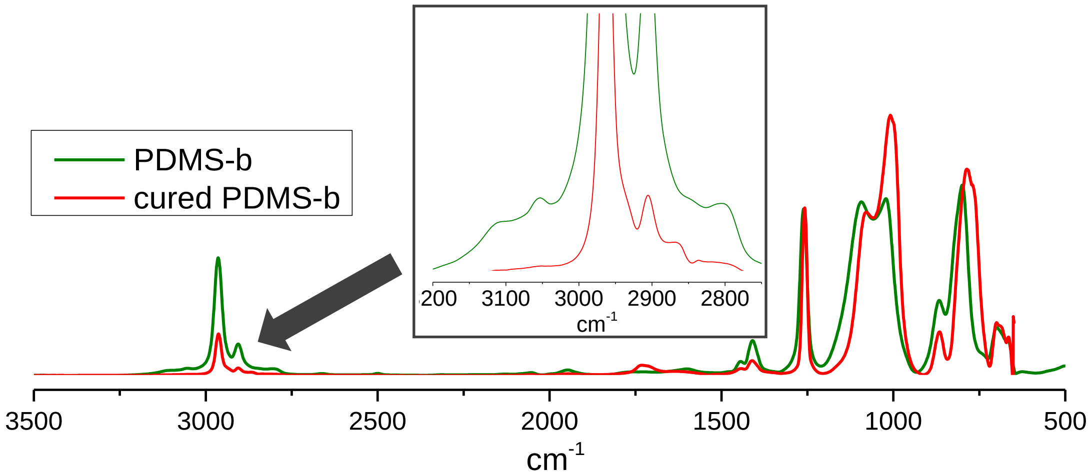


Fig. S1. The IR spectra of PDMS-b (*green curve*) and cured PDMS-b using peroxide **1** (*red curve*) (0.15 M).

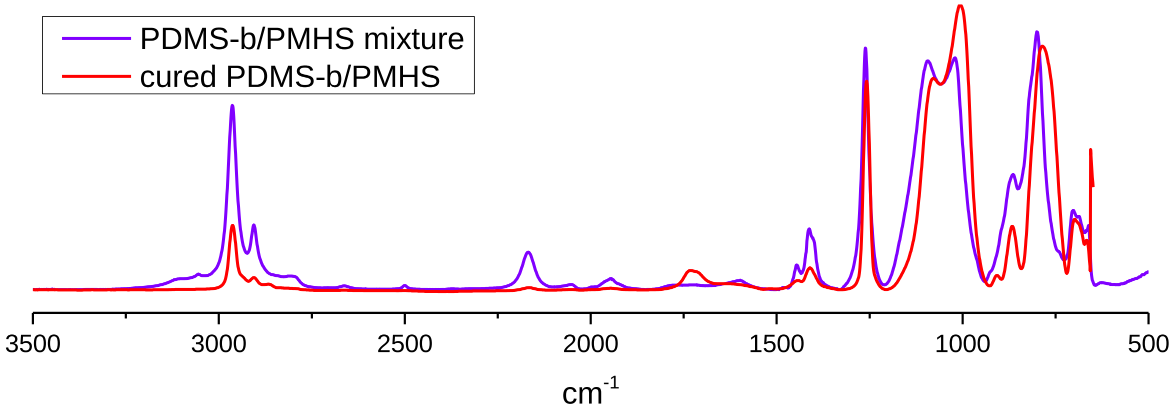


Fig. S2. The IR spectra of PDMS-b/PMHS mixture (*violet curve*) and cured PDMS-b/PMHS-rubber using peroxide **1** (*red curve*) (0.15 M).

1.3 DSC data

Table S2 Parameters of the free-radical induced silicone curing (peroxide concentration is 0.15 M)

Peroxide	Curing system	DSC data			
		T_{onset}, °C	T_{peak}, °C	T_{endset}, °C	ΔH, J/g
1	PDMS-b	163	190	208	−65.5
	PDMS-b/PMHS	165	186	205	−73.8
2	PDMS-b	167	192	209	−71.4
	PDMS-b/PMHS	168	191	209	−77.8
DBP	PDMS-b	93	119	145	−6.2
	PDMS-b/PMHS	93	124	139	−5.2

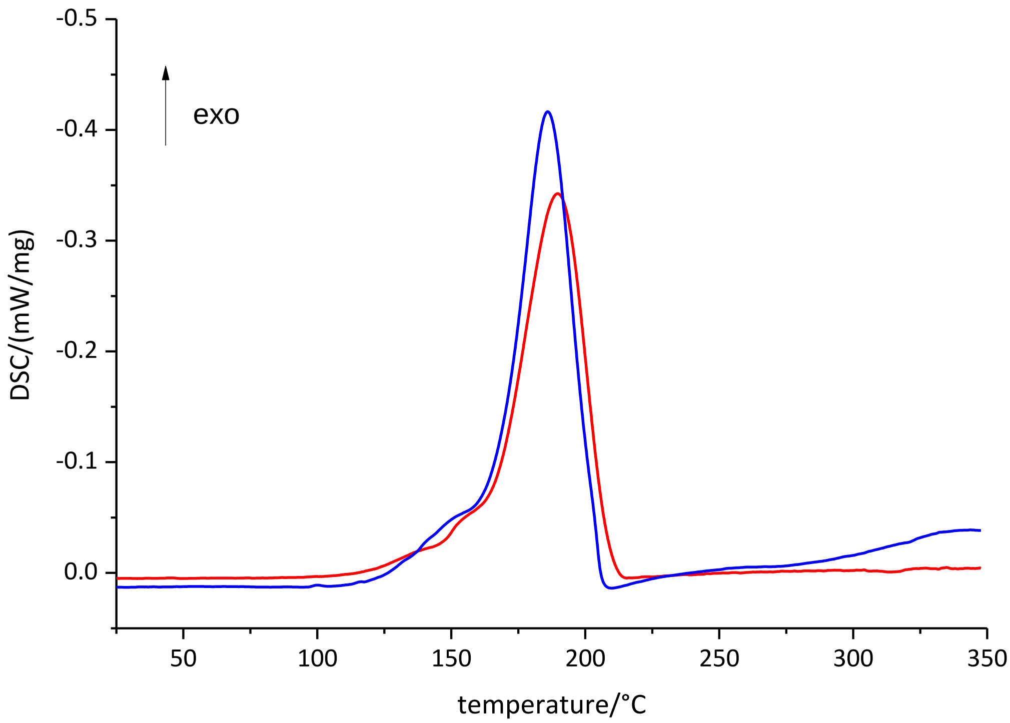


Fig. S3. DSC curves of the curing initiated by peroxide **1** (0.15 M): PDMS-b (*red curve*) and PDMS-b/PMHS mixture (*blue curve*).

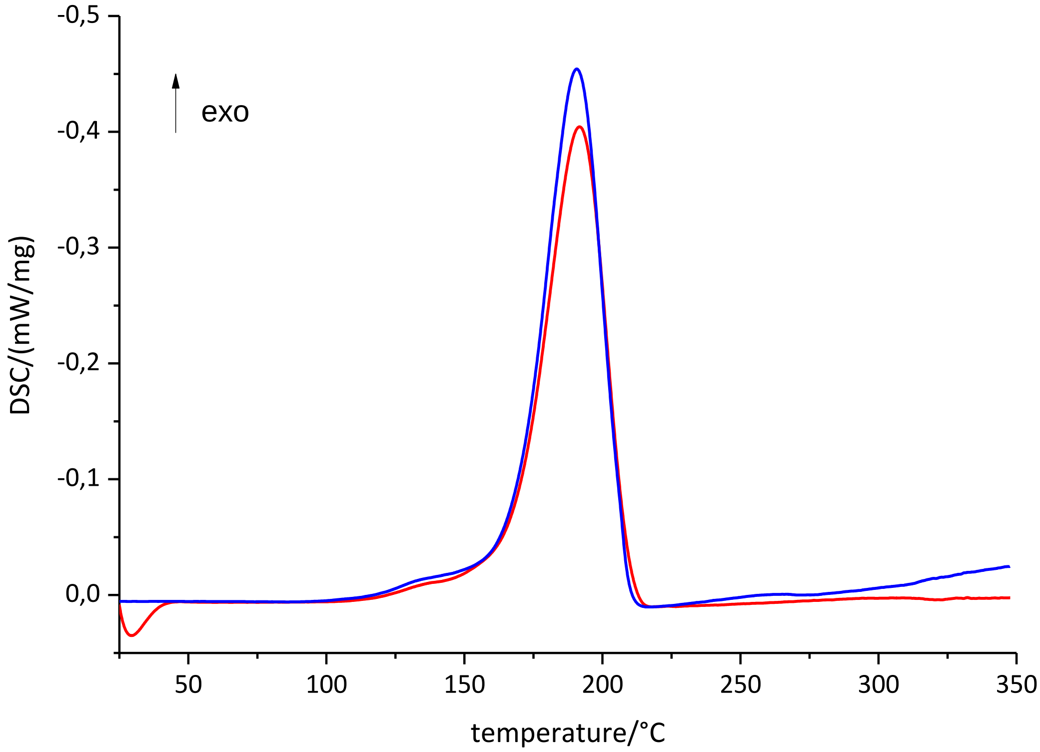


Fig. S4. DSC curves of the curing initiated by peroxide **2** (0.15 M): PDMS-b (*red curve*) and PDMS-b/PMHS mixture (*blue curve*).

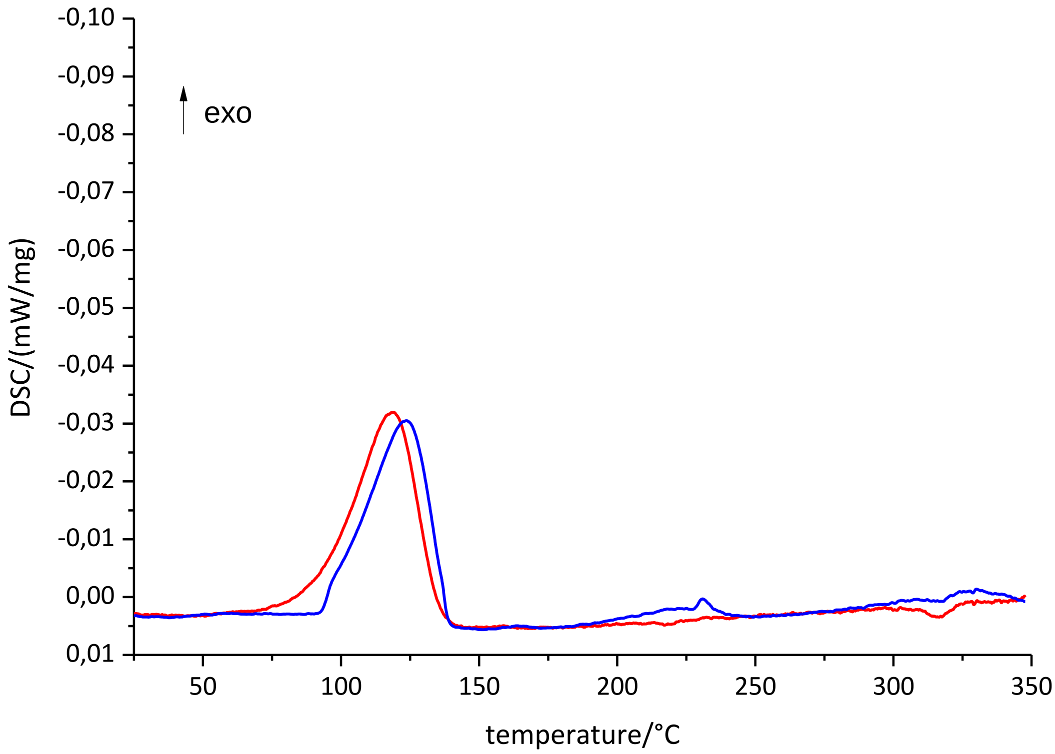
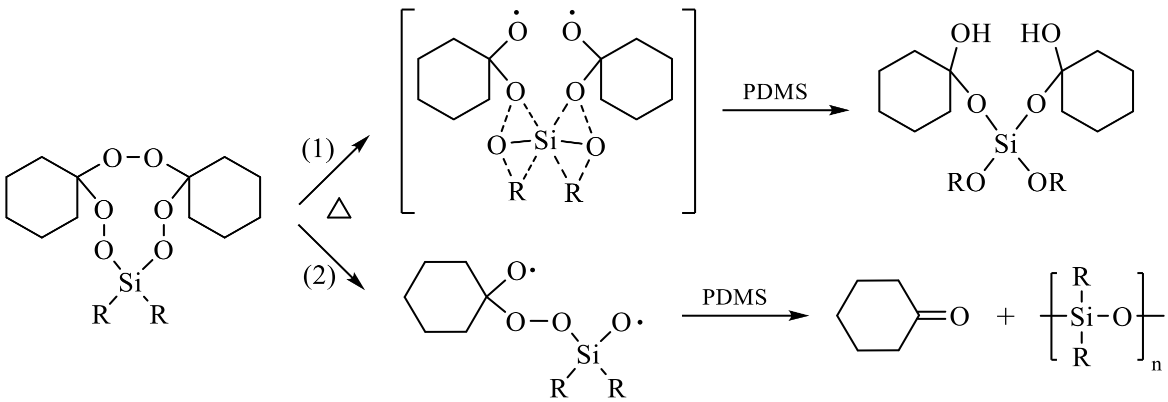


Fig. S5. DSC curves of the curing initiated by DBP (0.15 M): PDMS-b (*red curve*) and PDMS-b/PMHS mixture (*blue curve*).

II. Solubility of 1,2,4,5,7,8-hexaoxa-3-silonanes in PDMS

1–**2** dissolve far better in liquid PDMS under RT with thorough stirring than dibenzoyl peroxide (DBP). **3** is highly soluble in PDMS without experiencing any difficulties. DBP and **4** only dissolve in liquid PDMS by being heated up to 100 °C with thorough mixing, which makes it difficult to prepare liquid curing mixtures. This fact makes these cyclic organosilicon peroxides more suitable for the preparation of homogeneous curing mixtures based on polysiloxanes.

III. Thermal decomposition of 1,2,4,5,7,8-hexaoxa-3-silonanes



Scheme S1. Possible decomposition mechanisms of 1,2,4,5,7,8-hexaoxa-3-silonanes.

IV. Thermal properties of cured silicone rubbers

The temperature of the decomposition's beginning of PDMS-b- and PDMS-b/PMHS-rubbers, obtained by curing with cyclic organosilicon peroxides **1–2** at different concentrations (0.03–0.15 M) does not change and lies within 200–250 °C (as in case of DBP). However, all silicone rubbers cured by **1–2** are more thermally stable (on average by around 25–50 °C) than samples obtained using DBP (Fig. S6).

The rubbers obtained from PDMS-b/PMHS mixtures using **1** have the increased temperature of the decomposition's end (on average by 25 °C) and the increased residual mass (on average by 5–10%) in compassion with PDMS-b-rubbers cured by **1** (Fig. S7). Accordingly, for PDMS-b and PDMS-b/PMHS-rubbers cured by **1** the residual masses range from 25±5% to 35±5% at 800 °C in air. On the contrary, in case of DBP the use of silicone hydride does not affect the thermal properties of the product, and residual masses of vulcanizates at 800 °C are 25±5% of the initial mass.

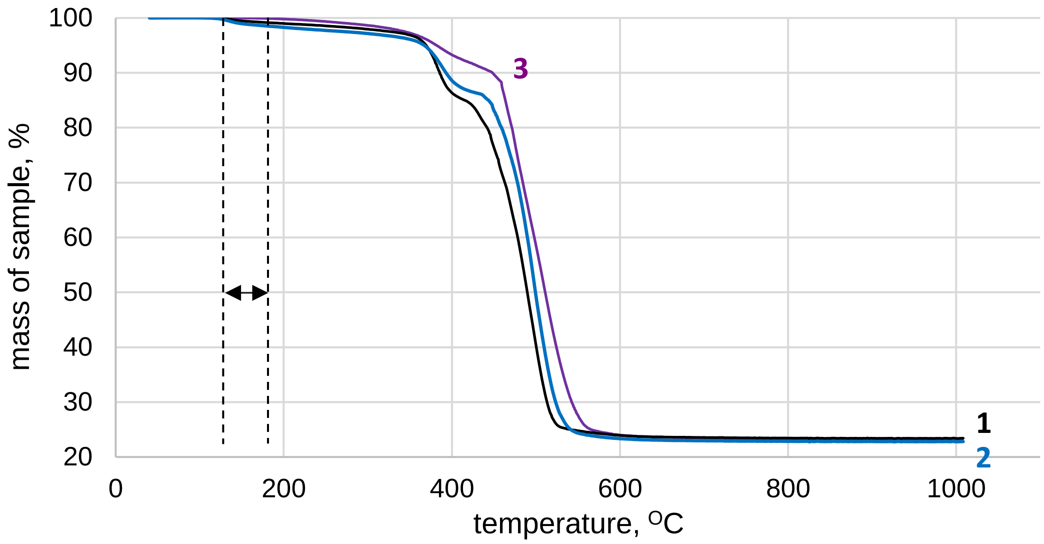


Fig. S6. Thermal degradation of silicone rubbers obtained from PDMS-b: 1 – 0.03 M DBP, 2 – 0.03 M DBP with an additive of PMHS, 3 – 0.03 M peroxide **1**.

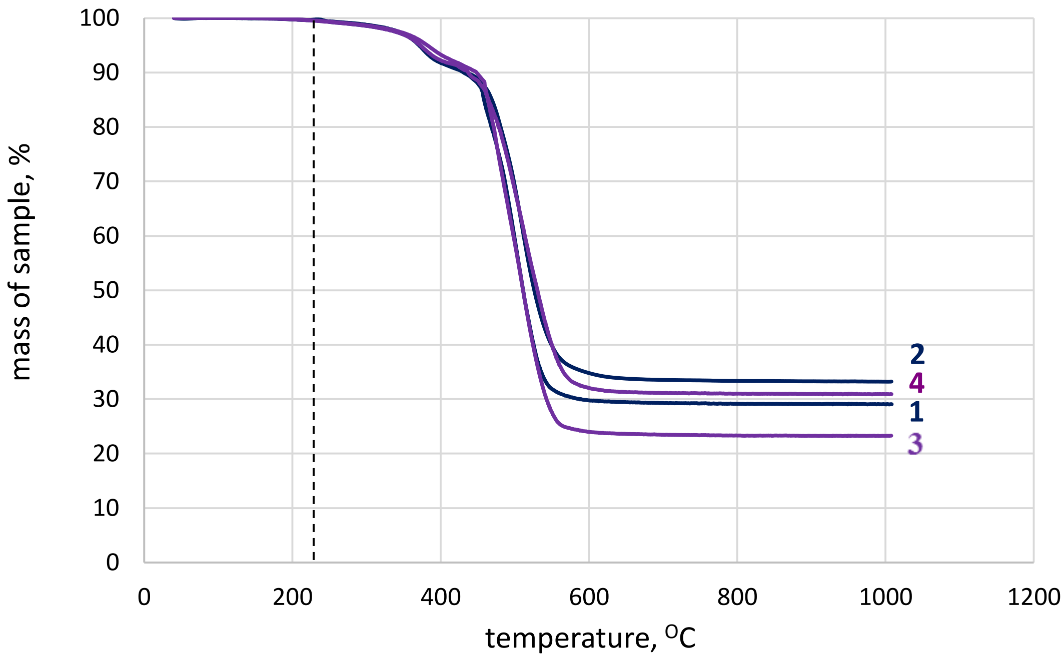


Fig. S7. Thermal degradation of samples: 1 – PDMS-b with 0.15 M **1**, 2 – mixture PDMS-b/PMHS with 0.15 M **1**, 3 – PDMS-b with 0.03 M **1**, 4 – mixture PDMS-b/PMHS with 0.03 M **1**.

V. Swelling properties of cured silicone rubbers

Table S3. Swelling properties of obtained silicone rubbers (concentrations of peroxides are 0.15 M).

Curing system	Curing agent	Swelling, %	w_{sol}, %	υ
PDMS-b	**1**	448	16.8	0.17
PDMS-b	**2**	452	17.0	0.18
PDMS-b	DBP	360	15.2	0.22
Mixture PDMS-b/PMHS	**1**	371	9.5	0.23
Mixture PDMS-b/PMHS	**2**	448	10.5	0.23
Mixture PDMS-b/PMHS	DBP	358	11.2	0.22

VI. Mechanical properties of cured silicone rubbers

6.1 Elastic properties

Table S4. The average values of the stress at rupture of cross-linked silicone rubbers obtained with the use of **1–2** and DBP, and their maximum tensile strain.

Curing system	Peroxide	Concentration of peroxide, M	σ, MPa	L, %	Δl, %
PDMS-b	**1**	0.15	0.02	188	8
PDMS-b	**1**	0.22	0.03	154	8
PDMS-b	**2**	0.15	0.04	169	6
PDMS-b	DBP	0.15	0.06	144	10
PDMS-b	DBP	0.22	0.05	124	10
Mixture PDMS-b/PMHS	**1**	0.15	0.17	203	5
Mixture PDMS-b/PMHS	**1**	0.22	0.16	201	3
Mixture PDMS-b/PMHS	**2**	0.15	0.15	212	3
Mixture PDMS-b/PMHS	DBP	0.15	0.08	154	5

Mixture PDMS-b/PMHS	DBP	0.22	0.05	139	5

σ – tensile strength; L – the percentage elongation, Δl – the residual elongation.

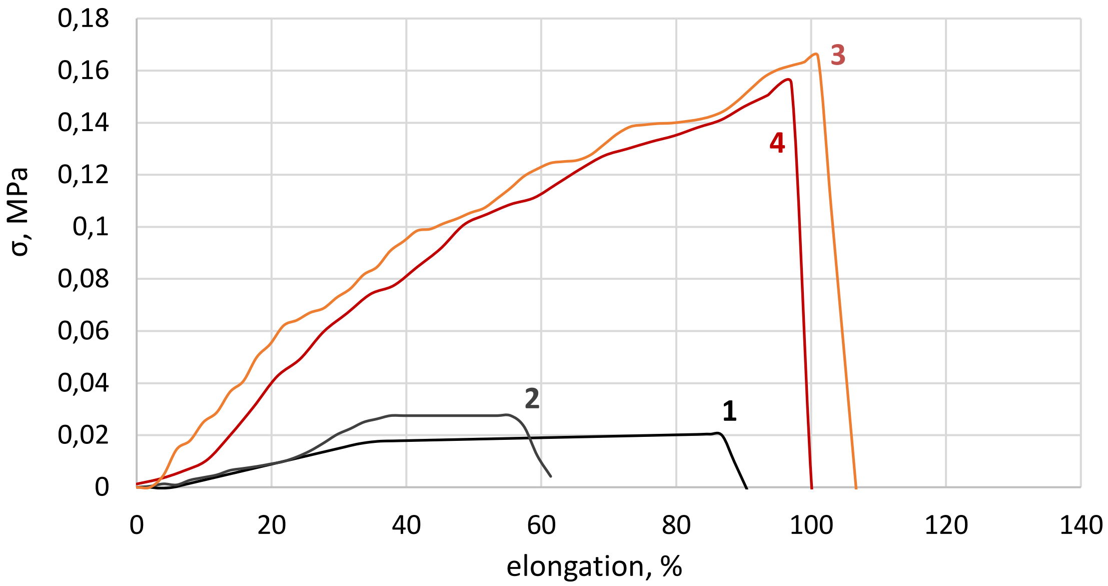


Fig. S8. Stretch diagrams of vulcanizates obtained by peroxide curing using peroxide **1** at 180 °C: 1 – PDMS-b cured by **1** 0.15 M, 2 – PDMS-b cured by **1** 0.22 M, 3 – PDMS-b/PMHS cured by **1** 0.15 M, 4 – PDMS-b/PMHS cured by **1** 0.22 M.

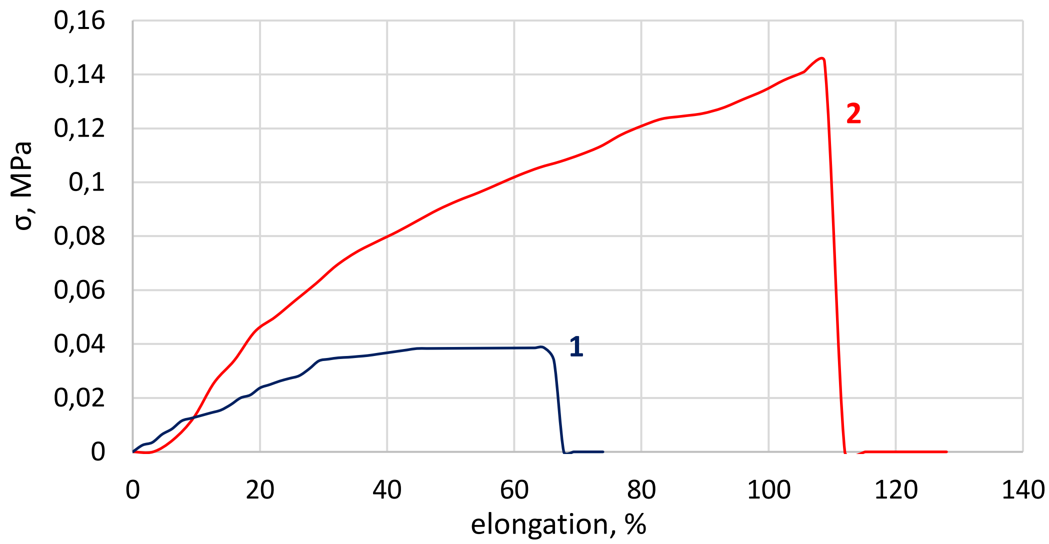


Fig. S9. Stretch diagrams of cross-linked silicone rubbers obtained by peroxide curing from PDMS-b using peroxide **2** at 180 °C: 1 – PDMS-b cured by **2** 0.15 M, 2 – PDMS-b/PMHS cured by **2** 0.15 M.

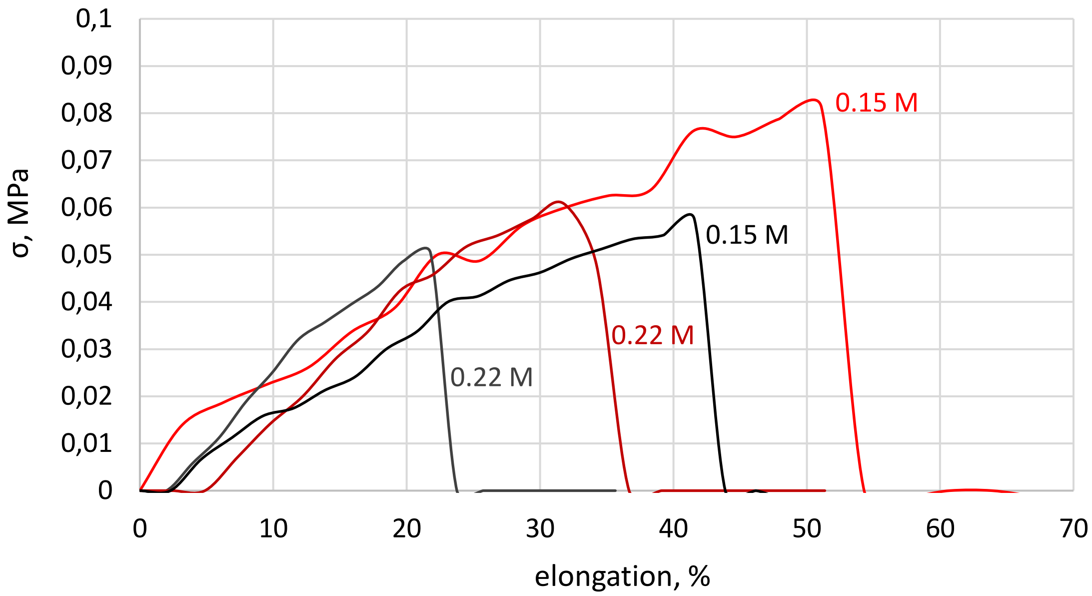


Fig. S10. Stretch diagrams of vulcanizates obtained by peroxide curing from PDMS-b using DBP at 110 °C. Graphs of samples without an additive of PMHS are highlighted in black, those in red with an additive of PMHS. Concentrations are shown in M.

6.2 Compression properties

Table S5. Compression characteristics of obtained silicone rubbers.

Curing system	Peroxide	Concentration of peroxide, M	σ, MPa		Compression set, %
			20%	40%	
PDMS-b	**1**	0.03	0.02	0.09	2.0
PDMS-b	**1**	0.09	0.04	0.14	1.9
PDMS-b	**1**	0.15	0.04	0.16	2.0
PDMS-b	**2**	0.09	0.04	0.14	3.7
PDMS-b	**2**	0.15	0.05	0.19	3.0
PDMS-b	DBP	0.03	0.05	0.19	5.3
PDMS-b	DBP	0.15	0.06	0.27	6.8
Mixture PDMS-b/PMHS	**1**	0.03	0.07	0.20	1.3
Mixture PDMS-b/PMHS	**1**	0.09	0.11	0.39	0
Mixture PDMS-b/PMHS	**1**	0.15	0.09	0.40	1.0
Mixture PDMS-b/PMHS	**2**	0.09	0.06	0.30	0
Mixture PDMS-b/PMHS	**2**	0.15	0.11	0.39	0.8
Mixture PDMS-b/PMHS	DBP	0.03	0.04	0.18	5.7
Mixture PDMS-b/PMHS	DBP	0.15	0.05	0.26	7.4

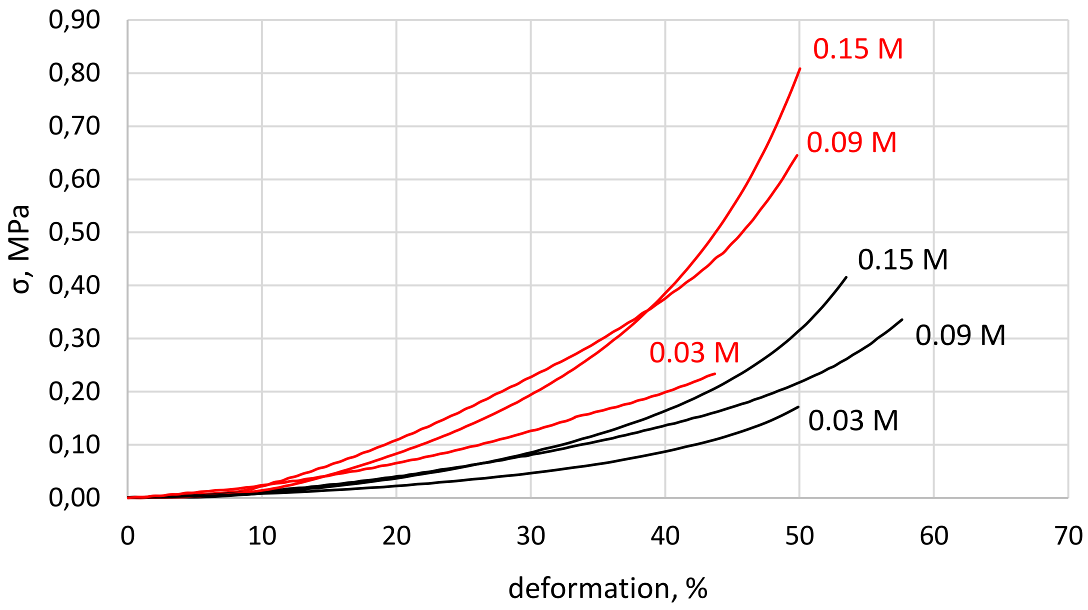


Fig. S11. Compression diagrams of silicone rubbers obtained by peroxide curing from PDMS-b using peroxide **1** at 180 °C. Graphs of samples without an additive of PMHS are highlighted in black, while those with an additive of PMHS are in red. Concentrations are shown in M.

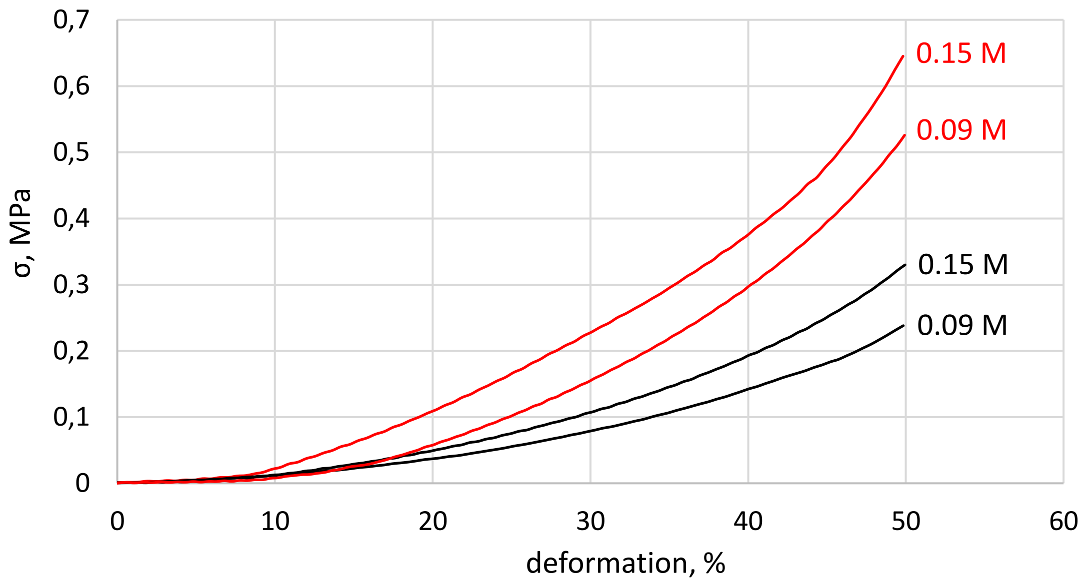


Fig. S12. Compression diagrams of silicone rubbers obtained by peroxide curing from PDMS-b using peroxide **2** at 180 °C. Graphs of samples without an additive of PMHS are highlighted in black, while those with an additive of PMHS in red. Concentrations are shown in M.

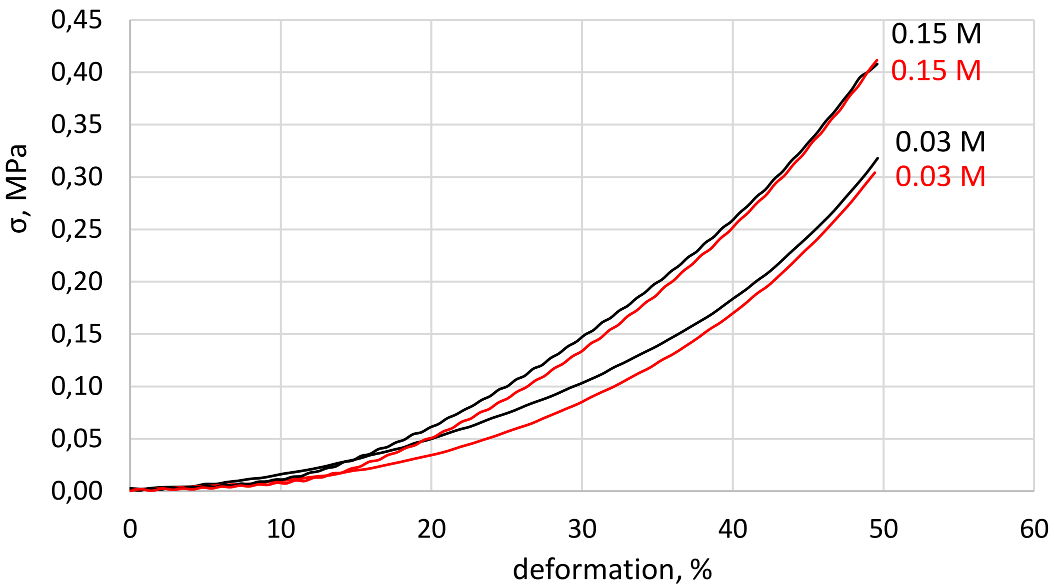


Fig. S13. Compression diagrams of vulcanizates obtained by peroxide curing from PDMS-b using DBP at 110°C. Graphs of samples without an additive of PMHS are highlighted in black, while those with an additive of PMHS are in red. Concentrations are shown in M.

VII. Antibacterial properties of cured silicone rubbers

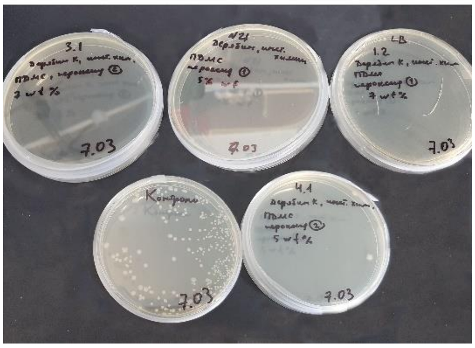


Fig. S14. Forming of colony forming units (CFU) Escherichia coli in the Petri dishes with nutrient medium after incubation of bacterial suspension on silicone samples.