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SUPPLEMENTARY INFORMATION for:

ALL-SILICONE ELASTIC COMPOSITES WITH COUNTER-INTUITIVE PIEZOELECTRIC RESPONSE, DESIGNED FOR ELECTROMECHANICAL APPLICATIONS

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Figure S1: Cl-modified silicone mixed with PDMS and cross-linked together (left) versus PDMS –polar particles composite film (right)

Infrared spectroscopy

The cyclic nature of CMV compound was supported by the absence of Si-OH band at 3690 cm^{-1} in the FT-IR spectrum as well as by the shape of the siloxane band (Figure S2). It is well-established that cyclic trimers have an absorption band at 1010-1020 cm^{-1}, cyclic tetramers and pentamers at 1070-1090 cm^{-1}, while for larger compounds the Si-O-Si band widens and splits.[S1] In our case, the shape and position of the Si-O-Si band, at 1076 cm^{-1} point towards a tetramer majority species, which is in agreement with H NMR (Figure S3). The $Si(CH_3)$ bands are at 1261, 808 and 852 cm^{-1}, while the $Si-CH=CH_2$ specific bands were found at: 961 and 1011 cm^{-1}, 1408 and 1599 cm^{-1}. After photo-addition, the bands

corresponding to the vinyl group disappeared and weak bands are observed at 1420 and 2852 cm^{-1} that could be assigned to (S-)CH_2 bonds (stretch asymmetric and δ, respectively).[S2]

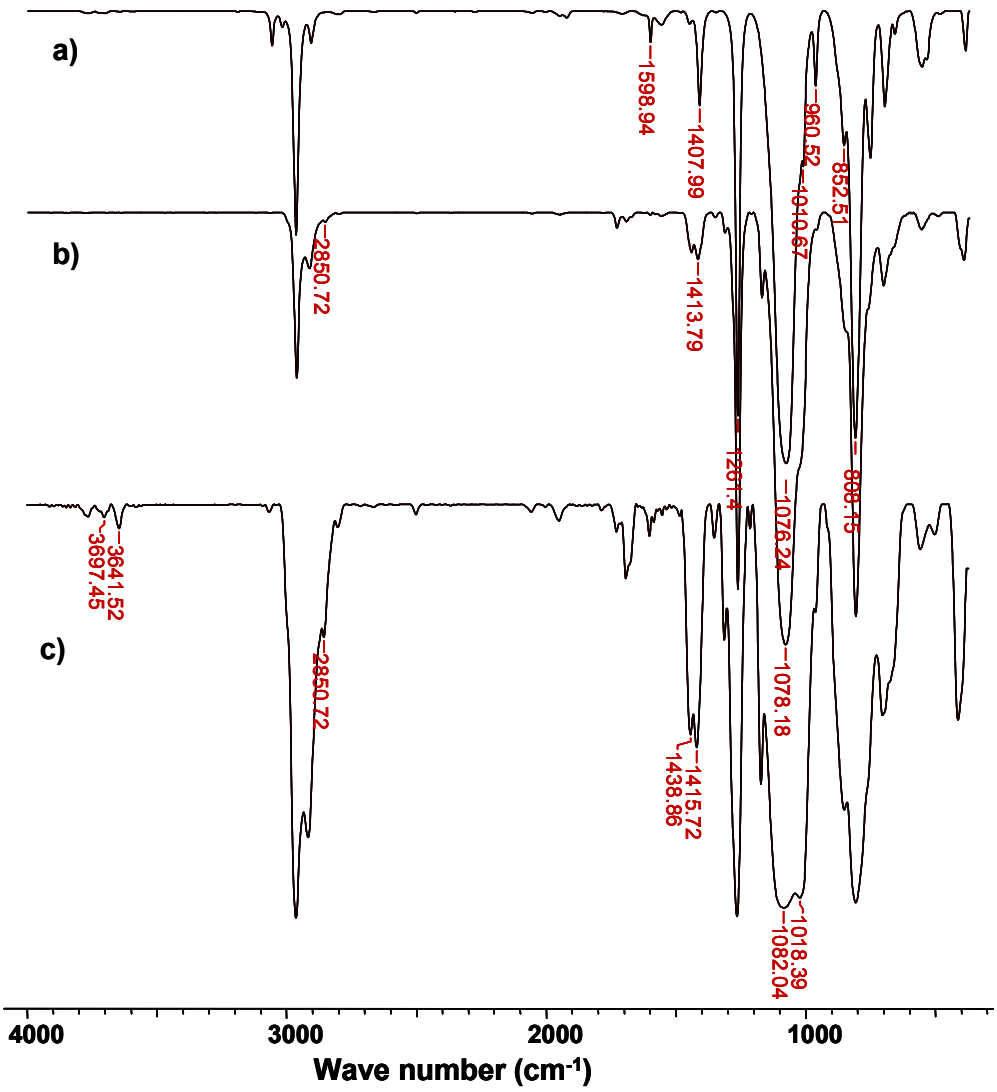

Figure S2: FT-IR spectra of CMV (a), Cl-23 (b) and Cl-33P (c)

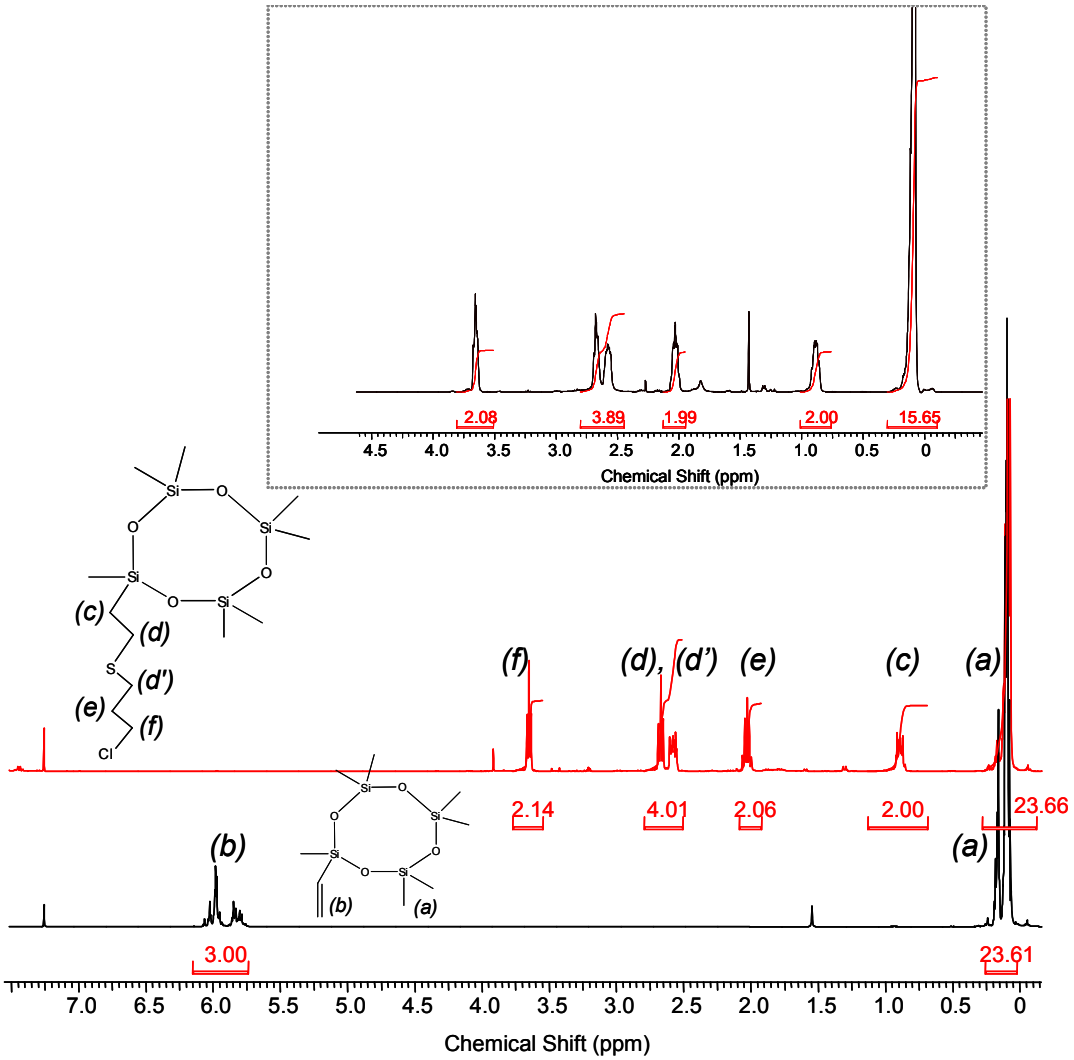

Figure S3: H NMR spectrum of methyl-vinyl cyclosiloxane (bottom), Cl-23 (up) and the corresponding copolymer Cl-33P (inset)

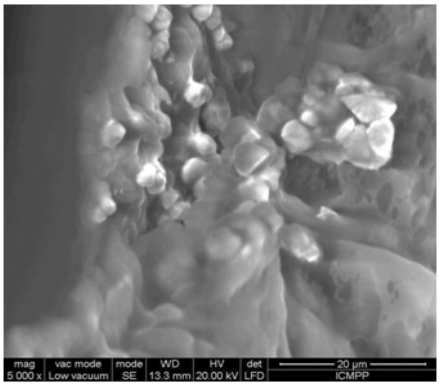

Figure S4: SEM image of a composite having PDMS matrix and a siloxane copolymer with 62 mol% CN groups as particles stabilized with a siloxane surfactant

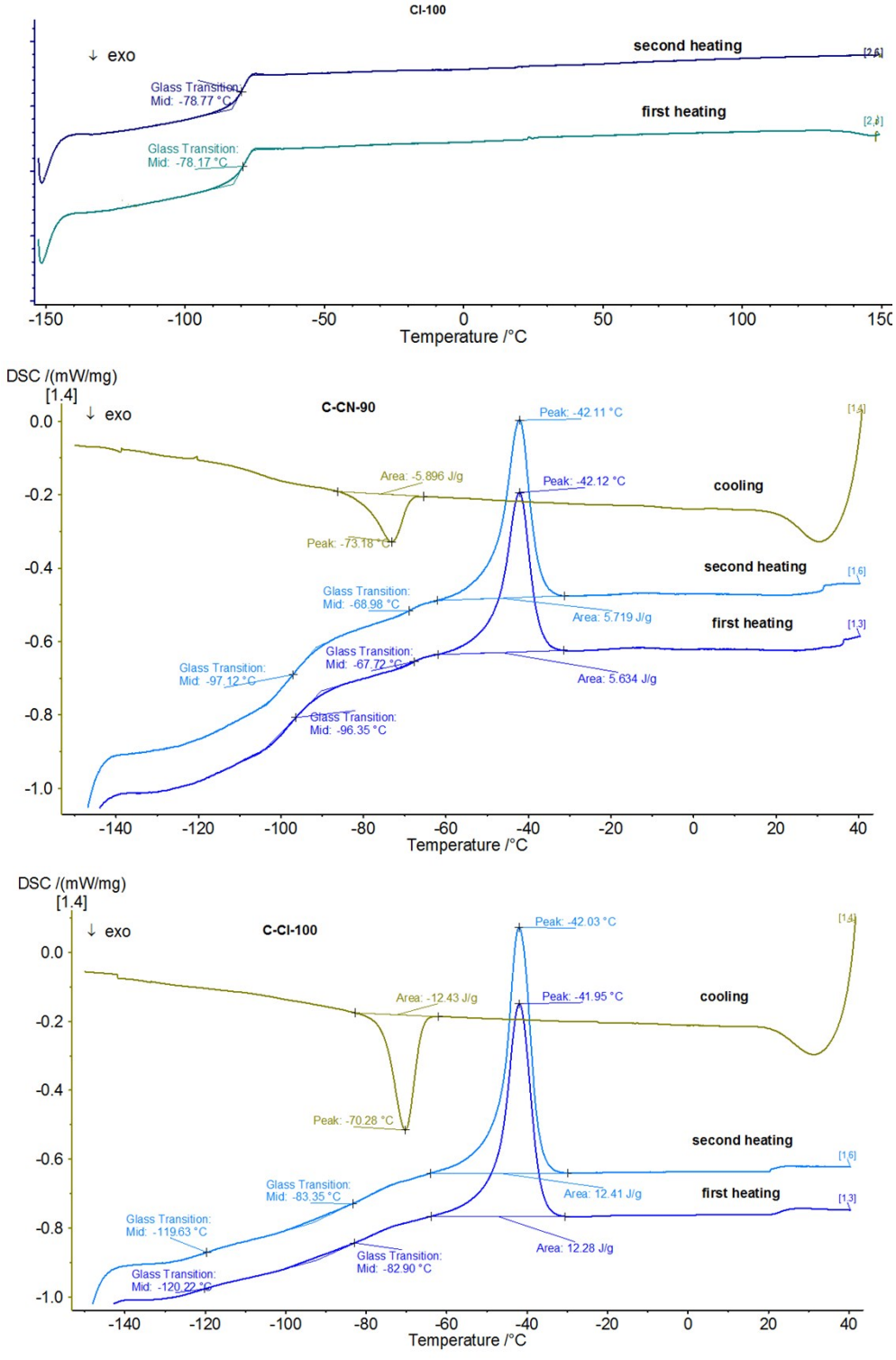

Figure S5: DSC curves of Cl-100 and composites C-CN-90 and C-Cl-100

Table S1: Calculated solubility parameters and density[S3] of the components of all-silicone composites

Code	Cl-23	Cl-100	CN-25	CN-90	Pluronic L81	PDMS
δ, $(cal \cdot cm^{-3})^{0.5}$	8.05	9.24	8.01	9.46	10.21	7.4
d, $g \cdot cm^{-3}$	1.0086	1.1144	0.9515	1.0335	1.1048	0.97*

* According to ref.[S4]

The complex dielectric permittivity at room temperature was recorded by sweeping frequency from 0.1 to 10^6 Hz, using a Novocontrol Dielectric Spectrometer equipped with frequency response analyzer. For measuring liquid samples the polymer was pressed between two electrodes (Ø = 20 mm) while the samples thickness was adjusted with glass spacers to140 μm and the material in excess was removed. The free-standing films were sandwiched between two gold-platted electrodes (Ø = 20 mm) and the analyses have been carried out in dry nitrogen atmosphere. For variable temperature measurements, the Quatro Cryosystem has been used in order to set the temperature of the analyzed sample with 0.1°C stability within the range of -150°C – 40°C.

The **effective dielectric constant** of a heterogeneous dielectric with two phases is estimated as:

$$\varepsilon^n_{eff} = v_1\varepsilon_1^n + v_2\varepsilon_2^n \qquad (1)$$

where ε_1 and ε_2 are the dielectric permittivity of the phases (matrix and filler, respectively), v_1 and v_2 are the volume fractions, n is the structural index of the mixture ($-1 \leq n \leq 1$).[S5,S6] The lower and upper limits of dielectric permittivity of the composite may be expressed as:

$$\varepsilon_{min} = v_1\varepsilon_1 + v_2\varepsilon_2 \qquad (2)$$

$$\varepsilon_{max} = \varepsilon_1\varepsilon_2 / (v_2\varepsilon_1 + v_1\varepsilon_2) \qquad (3)$$

The volume fractions were calculated using density data from Table S1.

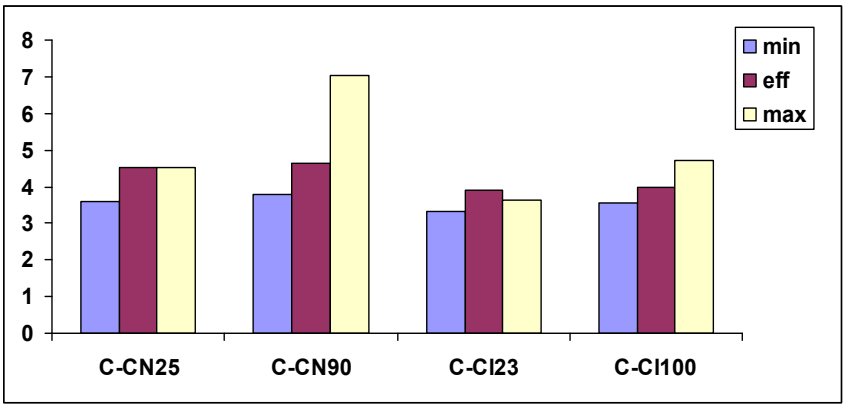

Figure S6: Dielectric constant of the composites measured at 10 kHz (ε_{eff}) and its limits calculated with the mixing rule

The Havriliak- Negami equation:[S7]

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau_{HN})^a]^b} \qquad (4)$$

where $\Delta\varepsilon=\varepsilon_s - \varepsilon_\infty$ represents the intensity of relaxation, i.e., the difference between the real permittivity values at the low ($\omega\rightarrow 0$) and respectively, high ($\omega\rightarrow\infty$) frequency limits, $\omega=2\pi f$ represents the angular frequency, f is the frequency, τ is the relaxation time for each process associated with peak maxima, and a and b represent the broadening and skewing parameters, respectively. WinFIT software provided with Novocontrol dielectric spectrometer was used for data fit.

Piezoelectric force microscopy (PFM) technique was employed for quantitative determination of the longitudinal piezoelectric coefficient d_{33} using a multimode AFM microscope (NT-MDT SolvePro) equipped with a PFM measurement option. Microscope controlling, acquisition and analysis of the data were done by using *Nova* software. **PFM** technique is able to use inverse piezoelectric effect to obtain local polarization of electric dipoles. PFM technique is based on the detection of the local electromechanical vibration of the sample caused by an external alternating voltage applied between the conductive AFM-tip and the investigated sample. The external electric field causes a piezoelectric deformation of the material underneath the tip, both out-of-plane and in-plane. The out-of-plane deformation is measured by the deflection of the cantilever, while in-plane deformation is measured by torsion of the cantilever. In this experiment, only out-of-plane deformation was measured, which allows to determine only the longitudinal piezoelectric coefficient d_{33}. All PFM images were taken during one imaging session with the same cantilever (nominal spring constant 2.8

$N \cdot m^{-1}$ and free resonant frequency of 197.2 kHz) and laser position in order to allow for quantitative comparison across the samples investigated. PFM measurements (surface topography, phase and amplitude of piezoresponse) over surface area 20×20 μm^2, were performed in contact mode, in air, at room temperature, using vertical set-point deflection of 2 nm, amplitude AC voltage of 1 V and scanning speed of 0.8 Hz. The average value of the longitudinal piezoelectric constant (d_{33}) was evaluated by recording piezoresponse curves in 100 equidistant points placed over five random surfaces with size area of 20×20 μm^2. The piezoresponse curves were obtained by sweeping DC bias voltage and the piezoelectric constant was calculated from the slope of the linear dependence of piezoresponse amplitude on bias voltage.

References

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