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All-silicone elastic composites with counter-intuitive piezoelectric response, designed for electromechanical applications†

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New all-silicone composite materials were prepared using polar silicone particles dispersed within a high molecular weight polydimethylsiloxane (PDMS) matrix. Polar silicones with either CN or Cl groups attached to the polysiloxane chain in similar proportions were prepared by appropriate post-polymerization reactions and submicron particles were obtained and stabilized with a hydrophobic commercial surfactant, Pluronic L81, while the polar polymers were cross-linked within the particles in most cases. The mechanical and dielectric properties of the all-silicone composites were measured and discussed as a function of the nature and number of polar groups in the filler particles and in correlation with morphological aspects. Soft elastomeric materials with a Young's modulus of 0.12–0.5 MPa, dielectric permittivity up to 4.7 at 10^4 Hz and dielectric strength up to 63 V μm^{-1} were obtained, and promising electromechanical performance resulted from theoretical calculations. Dielectric relaxation spectrometry at varying temperatures revealed dynamic relaxations in agreement with DSC data, and high dielectric relaxation strength values ($\Delta\varepsilon$) were calculated. We also report for the first time piezoelectric behaviour of all-polymer composites containing amorphous components, measured using Piezoelectric Force Microscopy (PFM) at ambient temperature (above T_g) without poling. Average longitudinal piezoelectric coefficients (d_{33}) of 24 and 13 pm V^{-1} were found for composites with cyano- and chloro-silicones, respectively. The variation of d_{33} with stretching was also followed and explained in correlation with morphological aspects. The promising properties of the all-silicone composites create the premises for possible applications as stretchable electronics, including tactile sensors, acoustic transducers and wearable devices.

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Introduction

Materials suitable for energy conversion applications must cumulatively meet a series of criteria: high dielectric permittivity, low dielectric losses, high breakdown field, high elongation, low Young's modulus and low viscoelastic losses.[1] Polydimethylsiloxane (PDMS) and most of its copolymers are soft materials, liquids at room temperature, and must be chemically cross-linked to obtain free-standing films. After cross-linking, very good mechanical properties can be obtained; however, non-polar PDMS has a low dielectric permittivity, <3. Thus, silicones (in most cases PDMS-based elastomers) are largely used as matrices for dielectric elastomer transducers, which are filled with particles with high permittivity or piezoelectric response.[1,2]

The use of organic or polymeric polar or conductive components in another polymer matrix is a viable path towards materials with improved electromechanical properties. Depending on the method of preparation, the resultant materials are polymer blends, co-networks or composites. When the polymeric fillers are used as pre-synthesized particles, all-polymer composites result. Such materials with conductive polymers as filler particles – focusing on polyaniline (PANI) – have been prepared as a means to increase dielectric permittivity, and have been investigated for electromechanical properties.[3–5] PDMS was used as a matrix in blends with high dipole polymers[6–9] and also in all-polymer composites containing organic polymers as filler particles, specially designed for electromechanical applications.[10–13]

Polar silicones are good candidates as high dielectric permittivity materials. Several possible ways for the exploitation of such polymers have been investigated, including chemical modification of silicones,[1,8,9,14–19] blending of PDMS and polar silicones,[7,8] interconnected or semi-interpenetrated all-silicone networks,[20–22] or using polar cross-linkers for PDMS.[23–25]

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In particular, we previously focused on different approaches for combining cyano-modified silicones with high molecular weight PDMS, with the purpose of achieving materials with good actuation responses. To significantly increase the dielectric permittivity, the polar groups and/or polar silicone must be incorporated in as high amounts as possible, without sacrificing the mechanical properties. For example, when an OH-terminated cyanopropyl-modified copolymer was cross-linked with PDMS, an improvement in actuation performance was obtained.[9] Blends of trimethylsilyl-capped cyanopropyl copolymers and PDMS in comparable amounts lead to phase separation, a phenomenon that is very likely in similar systems, and it is responsible for the poor mechanical properties of the final materials. It could be controlled to a certain degree by cross-linking the polar component *via* an on-chain hydrolysis–condensation reaction, when only microscopic phase separation is observed.[20] To further reduce the size of the polar domains, we also tested the pre-formation of cross-linked polar silicone particles and their use as fillers for high M_n silicones.

In the present work, we used two types of polar silicone particles stabilized and cross-linked in toluene and dispersed in a non-polar PDMS matrix. The resultant materials were all-silicone composites which were investigated concerning the effect of the nature (either CN or Cl) and content of the polar group in the polymeric filler on dielectric and mechanical properties, as well as on the theoretical electromechanical performance of the final materials. To our knowledge, apart from our previous testing, this is the first report on materials formed of a silicone matrix and cross-linked polar silicone particles, as dielectric elastomers.[1]

We also report for the first time piezoelectric behaviour measured using the PFM technique on full silicone materials, without piezoelectric fillers and poling in the classical sense. The longitudinal piezoelectric coefficient d_{33} was measured at ambient temperature (*ca.* 100 °C above the glass transition of the polar fillers) and its evolution during stretching was also followed. In addition, we tried to correlate the final material properties with the morphology of the films induced by the use of a PEO–PPO–PEO copolymer as a stabilizer, since it is known that the interface in polymer composites has a strong influence on their properties.[1] Moreover, the role of Pluronic type surfactants in silicone materials was relatively scarcely investigated, except for oil/water polymerization systems,[26] while their behaviour in organic media or their influence in composites is less known.

Experimental

Materials and methods

The following reagents were used as received: trimethylsilyl-terminated poly(methylhydro)siloxane and 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) from Alfa Aesar, allyl cyanide, platinum divinyltetramethyldisiloxane complex (Pt(dvs)) solution in xylene (Karstedt catalyst), dibutyltin dilaurate (DBTDL), 3-chloro-1-propanethiol (CPT), 2,2-dimethoxy-2-phenylacetophenone (DMPA), dimethyldichlorosilane (DDS), methylvinyldichlorosilane (MVDS) and Pluronic L81 – a poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) with $M_n \sim 2800$ and 10 wt% poly(ethylene glycol) (HLB = 2), from Sigma-Aldrich; tetraethoxysilane (TEOS) from Fluka, octamethylcyclotetrasiloxane (D_4), hexamethyldisiloxane (HMDS) and tetramethyltetravinylcyclotetrasiloxane (V_4) from ABCR; and cation exchanger Purolite CT-175 – a macroporous styrene–divinylbenzene copolymer with sulfonic groups from Viromet S.A. Toluene for hydrosilylation was stored over molecular sieves and distilled from sodium wire prior to use.

The infrared spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer in transmission mode (32 scans, resolution 2 cm^{-1}) at ambient temperature. ^1H NMR spectra were recorded on a 400 MHz Bruker spectrometer in $CDCl_3$ without an internal standard. GPC measurements were made in chloroform on a GPC/SEC WGE 3010 (Brookhaven – Bures) after calibration with polystyrene standards.

For SEM investigation, the films were fractured in liquid nitrogen and the cross-section surface was examined using a Quanta 200 Environmental Scanning Electron Microscope (ESEM) operating at 20 kV with a large field detector. EDX qualitative analysis and mapping were done to emphasize the presence of Cl, S and N from the polar copolymers. TEM images and EDX analyses of the as-prepared polar particles were obtained using a Hitachi HT 7700 microscope. The particle dispersions in toluene were cast on Cu grids (300 mesh) and vacuum dried before analysis. DSC investigations were performed on a Pyris Diamond DSC (Perkin Elmer USA) instrument.

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 a frequency response analyzer and a Quatro Cryosystem for variable temperature measurements from −150 °C to 40 °C (please see ESI† for details). Breakdown strength measurements were performed in static mode on unstressed elastomeric films by applying a ramp signal of 100 V s^{-1} in the range 0–20 kV until the breakdown occurred.[27] Five measurements were made for each sample and the average value was calculated.

Stress–strain measurements were performed on dumbbell-shaped samples on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein, Germany. The measurements were run at an extension rate of 50 mm min^{-1} at room temperature. To evaluate the mechanical fatigue resistance, cyclic tests were performed: five cycles were run with a stationary time at maximum strength of 5 s, stationary time at minimum strength of 5 s, maximum strain of 100%, and minimum strain of 8%.

The 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 using Nova software (see ESI† for details).

Synthesis of the precursors

High molecular weight PDMS. An OH-terminated polydimethylsiloxane (PDMS), which was used as the matrix in the composites, was synthesized by ring-opening polymerization of D4 with H_2SO_4 as a catalyst.[28] M_n = 438 000 g mol^{-1}, PDI = 1.46.

Cyanopropyl-modified polysiloxanes. First, a trimethylsilyl-terminated poly(dimethyl-methylhydrogen)siloxane copolymer with 28.5% Si–H groups and M_n = 4200 g mol^{-1} was prepared in-house, with Purolite cation exchanger as a catalyst, according to previous reports.[29] The cyanopropyl-modified polysiloxanes (CN-90 and CN-25) were synthesized according to the general hydrosilylation procedure,[16,29] using allyl cyanide as the double bond reagent and either a poly(methylhydrogen)siloxane commercial homopolymer (M_n (NMR) = 2100 g mol^{-1}) or the poly(dimethyl-methylhydrogen)siloxane copolymer described above. By H NMR, un-reacted Si–H groups (10% and 3% mol, respectively) were found.

CN-25: H NMR in $CDCl_3$ (δ, ppm): 0.05–0.20 (Si–CH_3, 21H), 0.68 (NC–CH_2–CH_2–$C\underline{H}_2$–Si, 2H), 1.71 (NC–CH_2–$C\underline{H}_2$–CH_2–Si, 2H), 2.35 (NC–$C\underline{H}_2$–CH_2–CH_2–Si, 2H), 4.68 (un-reacted Si–H, 0.1H). M_n calculated ~5350 g mol^{-1}.

CN-90: H NMR in $CDCl_3$ (δ, ppm): 0.09–0.21 (Si–CH_3, 4H), 0.72 (NC–CH_2–CH_2–$C\underline{H}_2$–Si, 2H), 1.70 (NC–CH_2–$C\underline{H}_2$–CH_2–Si, 2H), 2.40 (NC–$C\underline{H}_2$–CH_2–CH_2–Si, 2H), 4.72 (un-reacted Si–H, 0.12H). M_n calculated ~4130 g mol^{-1}.

Chloro-modified polysiloxane (Cl-100). A ring-opening polymerization (ROP) reaction of V4 was carried out in bulk using Purolite CT-175 cation exchanger as a catalyst.[30] The next step was thiol–ene addition, which was adapted from the literature.[31] Methyl-vinyl polysiloxane and 3-chloro-1-propanethiol were used in stoichiometric amounts and dissolved in THF; then, a DMPA photo-initiator (5 wt%) was added. The solution was irradiated using a laboratory UV lamp at λ = 366 nm and RT under stirring, controlling the reaction from time to time by H NMR until there was complete disappearance of the vinyl proton signals, which took about 10 h. The modified polymer was recovered by precipitation in methanol. The molecular weight of Cl-100 was M_n = 5800 g mol^{-1}, PDI = 1.64.

H NMR in $CDCl_3$ (δ, ppm): 0.16 (Si–CH_3, 3H), 0.91 (–CH_2–Si, 2H), 2.04 (Cl–CH_2–$C\underline{H}_2$–$C\underline{H}_2$–S–, 2H), 2.58–2.68 (–CH_2–S–CH_2–, 4H), 3.66 (Cl–CH_2–, 2H).

Chloro-modified cyclosiloxane Cl-23 and the corresponding copolymer Cl-33P. First, methylvinylcyclosiloxane (CMV) was synthesized through a co-hydrolysis reaction.[32] In principle, dimethyldichlorosilane (DDS) and methylvinyldichlorosilane (MVDS) were added dropwise to a large excess of water under stirring at a temperature of 15–18 °C for 3 h. The organic phase was separated and washed repeatedly with water to remove HCl traces. Then, the hydrolysis product was subjected to depolymerization with 50% KOH aqueous solution and the volatile fraction formed was separated by distillation at 38–70 °C and 11 mmHg. The resulting mixture of cycles had a refractive index of $n_D{}^{20}$ = 1.4024 (compared with 1.396 for D4 and 1.405 calculated for heptamethyl vinylcyclotetrasiloxane). The H NMR spectrum showed an overall ratio of vinyl groups to dimethyl units of 1/3.3, which meant an average content of 23.2 mol% methylvinyl groups. In the second step, thiol–ene addition was performed on this compound as follows: 1.68 g (0.0152 mol) of 3-chloro-1-propanethiol, 5 g (0.0651 mol) of CMV and 0.25 g of DMPA were dissolved in THF and the solution was UV irradiated for 1 h, at λ = 366 nm and RT under stirring. The crude product was precipitated in methanol.

Cationic ROP of this modified cyclosiloxane was conducted in bulk with Purolite CT-175 cation exchanger as a catalyst for 10 h at 90 °C. The catalyst was filtered off and the cyclic by-products were removed at 160 °C and 10 mmHg. According to H NMR, the resulting copolymer contained 33% functional groups, and thus it was coded as Cl-33P. M_n = 21 800 g mol^{-1}, PDI = 1.8.

Preparation of all-polymer composites. First, the polar particles were prepared by stabilization in toluene using a hydrophobic surfactant, Pluronic L81, with concomitant cross-linking of the polar polymer within the particles where possible (CN-25, CN-90, Cl-100, and Cl-33P). An example follows. A mixture of 1.4 g of Cl-100 in THF (7 mL), 7 μL of dibutyltin dilaurate (DBTDL) solution (10 vol% in toluene) and 0.36 mL of tetraethyl orthosilicate (TEOS) was stirred in an open vessel for 30 min. This solution was injected into 14 mL of a 1% solution of Pluronic surfactant in toluene. When the cyclic compound Cl-23 was the polar component, no cross-linking agent was used in this step, since this reaction is not possible. In the case of CN-modified copolymers, to promote the hydrolysis of the un-modified Si–H groups, methanol was used before addition of TEOS and DBTDL, according to the protocol established previously.[20] In all cases, after mixing with the stabilizer, THF, methanol and about half the toluene were removed under vacuum.

In the second step, the as-obtained particle dispersion was mixed with 2.8 g of high M_n PDMS as a viscous toluene solution, containing the corresponding cross-linking agents, *i.e.* 0.64 mL of TEOS and 10 μL of DBTDL solution. After thorough mixing, films were cast on a Teflon substrate. These were peeled off after 24 h and kept under normal conditions for a week for maturation. The resultant materials, containing the same ratio between PDMS and polar copolymer (*i.e.* 2/1 wt) were coded as C-CN-*x* or C-Cl-*x*, where "*x*" stands for the molar percent of methyl-cyanopropyl or methyl-chloropropylthioethyl siloxane units in the polar component.

For comparison, a reference sample (coded as "PDMS") was obtained as follows: 0.5 g of PDMS was dissolved in 6 mL of a 1% solution of Pluronic L81 in toluene, and then 0.12 mL of TEOS and 5 μL of DBTDL solution (10% in toluene) were added and the solution was poured on a Teflon substrate. The resulting film was treated similarly with the composites.

Results and discussion

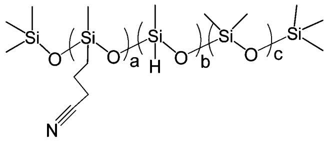
Polar silicones and submicron particles

Polar silicones, especially those with a high content of polar groups, have poor mechanical properties when cross-linked alone, while their blends with PDMS might need special care so as to avoid macroscopic phase separation. For example, mixing PDMS and the chloropropyl-modified silicone led to macroscopic phase separation (Fig. S1, ESI†) after cross-linking *via* chain-end condensation. As a way to reduce the phase separation to a microscopic scale, in previous work we obtained inter-connected polar–nonpolar networks[20] where cyano-copolymers were cross-linked through un-reacted Si–H groups. A more general path towards macroscopically unitary materials based on non-polar PDMS and polar silicones, which show acceptable mechanical properties, is to mix preformed cross-linked polar particles into a PDMS matrix. The as-obtained materials are all-polymer – in this case ''all-silicone'' – composites. Our approach involves the synthesis of polar silicones with cyano or chloro groups by appropriate chemical modification of hydrogen- or vinyl-containing polysiloxanes, their stabilization as particles and cross-linking, followed by mixing with the PDMS matrix.

Two cyanopropyl-modified polysiloxanes—one with the maximum possible content of CN groups that could be attached by hydrosilylation (CN-90) and one with a lower number of polar groups (CN-25)—were prepared[16,29] and used in this study (Scheme 1). The reminiscent Si–H groups were useful for subsequent cross-linking reactions within the particles.

For Cl-modified silicones Cl-100 and Cl-23, first a vinyl-containing homopolymer or cyclosiloxane, respectively, were obtained, followed by photo-addition of 3-chloro-propanethiol using DMPA as an initiator (Scheme 2).

The cyclic nature of the CMV compound was supported by the absence of a Si–OH band at 3690 cm^{-1} in the FT-IR spectrum as well as by the shape and position of the siloxane band, which, according to the literature,[33] indicates a tetramer majority species (please see details and spectra in ESI† Fig. S2) and is in agreement with H NMR (Fig. S3, ESI†). After photo-addition, the bands corresponding to the vinyl group at 961, 1011, 1408 and 1599 cm^{-1} disappeared and weak bands were observed at 1420 and 2852 cm^{-1} that could be assigned to (S–)CH$_2$ bonds (stretch asymmetric and δ, respectively).[34]



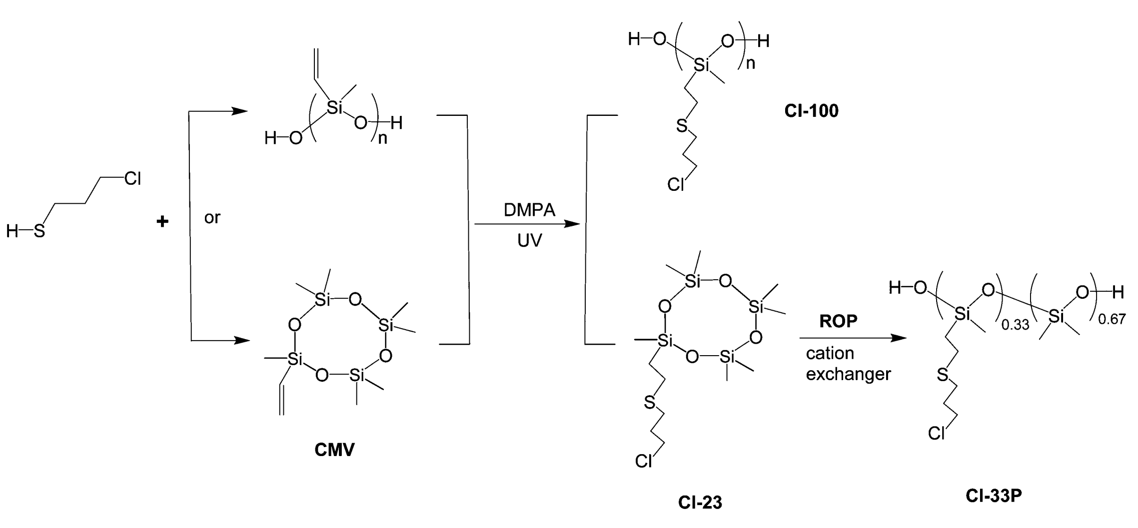
a = 0.90; b = 0.10 in CN-90
a = 0.25; b = 0.03; c = 0.72 in CN-25

Scheme 1

Chloro-modified cyclosiloxane was opened in the presence of a cation exchanger. The FT-IR spectrum of the polymerization product (Cl-33P) showed the modification and splitting of the Si–O–Si band, which was characteristic of a linear polysiloxane, together with absorption bands at around 3700 cm^{-1}, characteristic of OH chain ends (Fig. S2c, ESI†).

The H NMR of the chloro-modified silicones showed complete disappearance of the vinyl protons in the region 5.8–6.1 ppm and the presence of five sets of methylene protons (at ~0.9, 2.0, 2.5, 2.6 and 3.7 ppm) (Fig. S3, ESI†). After ring opening polymerization (ROP), the composition of the resultant copolymer was not identical to that of the starting cyclosiloxane, *i.e.* 33% functional groups were found on average (Fig. S3, ESI,† inset) as compared with 23% initially. This is not surprising, since ROP is accompanied by equilibration–redistribution reactions, resulting in cyclic compounds, which are subsequently removed. It seems that in this case, the removed species were mostly non-functional siloxanes, probably D3 and D4, which are more volatile.

Although the cyano- and chloro-modified silicones did not have exact matching composition, they were close enough to allow a fair comparison between samples prepared in the same manner. In addition, all the polar silicones had similar molecular weights, in the range of oligomers. The maximum modification degree in hydrosilylation with allyl cyanide was *ca.* 90%,[16] while complete modification of polysiloxane with Cl dipole was possible by thiol–ene addition. The chloro-modified cyclosiloxane was taken as a comparison term for CN-25, and it brought an additional parameter in our investigation, since it cannot be cross-linked like the other polar components. For comparison purposes, Cl-33P was also used in the following, since it derives from Cl-23 and can be cross-linked.



Scheme 2

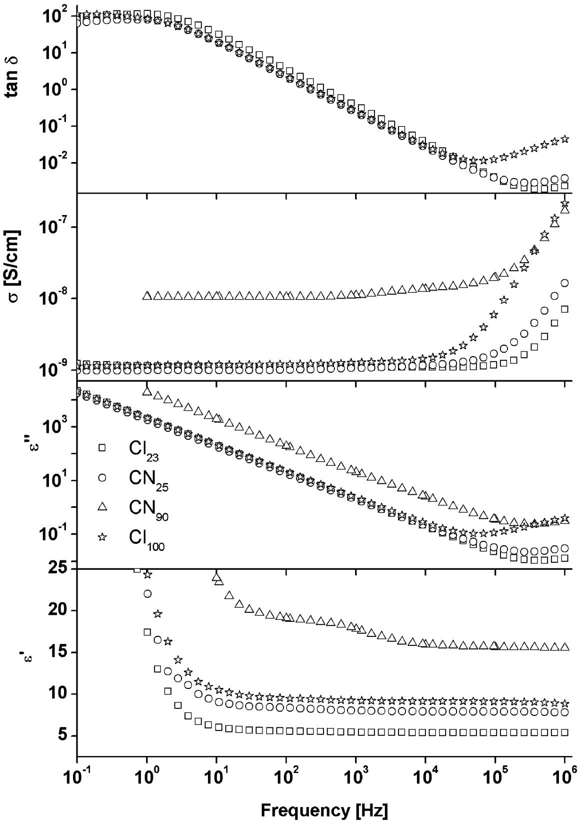


Fig. 1 Comparison of the dielectric properties of silicones modified with cyanopropyl and chloropropyl groups, respectively, in similar proportions (not cross-linked).

The most important reason for modification of silicones with polar groups was the expected increase in their dielectric constant. Therefore, we first compared the dielectric properties of the polar silicones, measured in the liquid state, without cross-linking (Fig. 1). The ε' values at 10 kHz were: 16 for the cyano-modified silicone (CN-90) and 9.2 for the chloro-modified homopolymer (Cl-100). When 100% modification with CN groups was done by thiol–ene addition[18] a maximum ε' value of 18 was reported, *i.e.* almost double that for 100% modification with Cl groups. For the copolymers with a lower substitution degree, the permittivity followed the same trend. When 25% CN groups were attached, ε' was 7.95 while for 23% Cl groups, ε' was 5.4 at 10 kHz.

The electrode polarization phenomenon was present in all cases but more pronounced in CN-modified polysiloxanes than in Cl-modified ones. Thus, at low frequencies, very high permittivity values were registered (Table 1), reaching 24.3 for Cl-100 and 175 for CN-90 at 1 Hz. Besides the increase of ε', the dielectric loss (ε'') and tan δ values were also high at low frequencies for all the samples. The conductivity was higher for CN-90 than for the other samples (Fig. 1). The nature of the dielectric loss was mainly conductive, with a linear dependence with logarithmic frequency, and in correlation with conductivity, where a stabilized plateau was observed below 10^5 Hz.

Most polysiloxanes have very low glass transition temperatures, *e.g. ca.* −120 °C for PDMS, so they are in the liquid state at room temperature, thus their particulate form is unstable. This can be solved by cross-linking the polymer core, with or without the addition of surfactants.[26,35,36] Although emulsions or dispersions of micron-size silicone particles have been long known in water, their production and behaviour in non-aqueous (organic) media has not been investigated much. In the present work, we used a hydrophobic commercial surfactant from the Pluronic class, which is soluble in toluene, this being the chosen solvent for the matrix polymer. The polar polysiloxanes were cross-linked in the presence of this surfactant, which acts mainly through steric stabilization.[26] The cross-linking may occur through –OH chain ends (in the case of Cl-100 and Cl-33P) or through on-chain –OH groups resulting after hydrolysis of un-reacted Si–H groups (for cyano-modified silicones). Conditions were created for these reactions to occur *in situ* in the toluene solution of the surfactant. It is generally known that solvents with a low dielectric constant, such as toluene, result in large particles,[37] but on the other hand an increased level of internal cross-linking makes the particles interface less deformable,[26] thus one can expect reduced coalescence.

In Fig. 2, a TEM image of the as-obtained Cl-33P submicron particles together with the corresponding EDX analysis is presented. The particle size is roughly between 250 and 450 nm (with a maximum at 350 nm), while the EDX on a line through a cluster of particles shows the presence of Si and Cl.

All-polymer composites with the PDMS matrix

PDMS is well known for its non-polar nature and incompatibility with most organic materials, and even with siloxane copolymers. In our previous work,[20] besides inter-connected networks of polar and non-polar silicones, we showed some preliminary comparative results on all-polymer composites. Particles of a cross-linked polar copolymer with cyano-propyl pendant groups were dispersed into the PDMS matrix, which was ultimately cross-linked in a similar way as described here. A siloxane-containing surfactant was used as a stabilizer for the particles, and the polar domain size in the composites was reduced by one order of magnitude as compared with the

Table 1 Dielectric properties of the polar silicones measured in the liquid state

	1 Hz				10 kHz			
Sample	ε'	ε''	σ (S cm^{-1})	tan δ	ε'	ε''	σ (S cm^{-1})	tan δ
Cl-23	17.4	2020	1.15×10^{-9}	116.0	5.4	0.218	1.09×10^{-9}	0.043
Cl-100	24.3	2050	1.16×10^{-9}	84.1	9.2	0.285	1.43×10^{-9}	0.031
CN-25	22.0	1750	9.95×10^{-10}	79.7	7.95	0.229	1.15×10^{-9}	0.029
CN-90	175.0	19 100	1.06×10^{-8}	109.1	16.0	2.72	1.36×10^{-8}	0.17

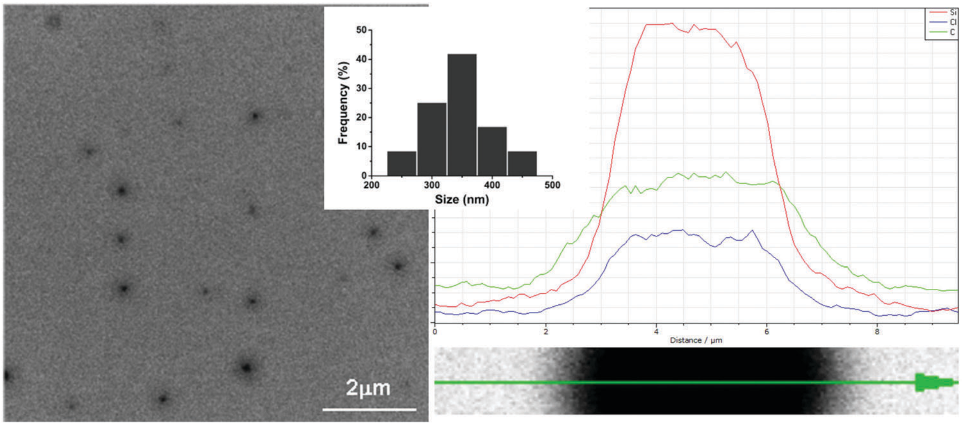


Fig. 2 TEM image, histogram and EDX analysis of the as-prepared Cl-33P particles.

spontaneous phase separation in the corresponding polar–nonpolar inter-connected networks. Here, we extended the research on all-silicone composites in order to establish a more general procedure. A PEO–PPO–PEO block copolymer (Pluronic L81) was used to stabilize the polar particles because of its commercial availability and convenient solubility in toluene. After cross-linking the polar polymers *in situ*, the particle dispersion was mixed with a high molecular weight PDMS (M_n = 438 000 g mol^{-1}) and the reagents for matrix cross-linking. The proportion between PDMS and the polar copolymer was kept constant, *i.e.* 2/1 (wt). After solvent evaporation, uniform and transparent thin films formed (an example is shown in Fig. S1, ESI†). A PDMS reference material containing a Pluronic admixture was specially designed to mimic the composites.

The morphology of the films was observed using SEM in cross-section (Fig. 3). Polar domains in the order of microns or even tens of microns were observed, which were much larger than the isolated single filler particles observed using TEM. These were probably agglomerates of polar particles covered by the surfactant and PDMS. It is known that neat PDMS has a very smooth and even aspect.[13] However, the reference film used here exhibited spherical domains which were probably Pluronic surfactant phase domains (Fig. 3a). A similar morphology with spherical aggregates was observed for a PDMS elastomer containing a PDMS–PEO stabilizer.[38] In the composite samples, variable dimensions of the domain size throughout the film thickness were noticeable, generally larger in the central region (Fig. 3b, f and i). The large size and polydispersity of the particles within the films were probably due to coalescence during slow evaporation of the solvent. This hypothesis was supported by further analysis of sample C-CN-90 using SEM on both surfaces (Fig. 3g and h), which revealed different morphology. One side showed particles relatively uniform in size and well dispersed within the film (Fig. 3h), while on the other side the dispersed objects looked like collapsed vesicles, larger than the particles (Fig. 3g). We suppose that this is a consequence of the concentration gradient during slow evaporation of the solvent from the film, corroborated with the slow cross-linking of the polar polymer, its higher density and the surfactant's behaviour in the un-friendly polysiloxane environment.

Comparing SEM observations with our previous data, it seems that better silicone-based materials in terms of morphology can be obtained with a siloxane-based surfactant. For example, smaller polar silicone particles with clear phase boundaries (Fig. S4, ESI†)[20] and more uniform dispersion of *in situ* synthesized polymer nanoparticles within the film thickness[13] were observed. The differences between the present composites and the previous ones were most likely due to the chemical nature of the stabilizer. In the case of a siloxane compound forming reverse micelles in toluene, the particle shell is formed by the siloxane backbone, which increases the compatibility between the matrix and the disperse phase. Instead, the organic surfactant extended the less polar PPO block in toluene forming the particle shell, while the PEO blocks remained inside the reverse micelles. Given the (methyl)siloxane backbone of both the disperse phase and the matrix, it is assumed that incompatibility between the Pluronic surfactant and the siloxane components would manifest, which would probably favor the formation of large aggregates after solvent evaporation. It has been shown that the adsorbed layer of (PEO–PPO–PEO) block copolymer surfactants on PDMS droplets dispersed in water have variable thicknesses, depending on the length of the blocks, and decreasing with the degree of internal cross-linking.[26] If we extend the reasoning to our case, given the fact that the particles were not separated after preparation, it is assumed that the un-adsorbed surfactant remained in the films and might have produced a separate phase or otherwise influenced the morphology. This hypothesis is supported by the completely different aspect of the composite obtained with Cl-23 cyclic siloxane (Fig. 3c and d) as compared with the other samples. In this particular case, the core material was not cross-linked, thus according to the literature, the surfactant layer adsorbed at the surface of the droplets would be thicker and the interface more deformable. Indeed, in this sample the disperse phase domains had an elliptical shape, while on close examination small and regular spherical particles were observed within these domains (Fig. 3d). When the copolymer with a similar composition was cross-linked within the particles, the all-silicone film morphology completely changed, as can be seen in Fig. 3e.

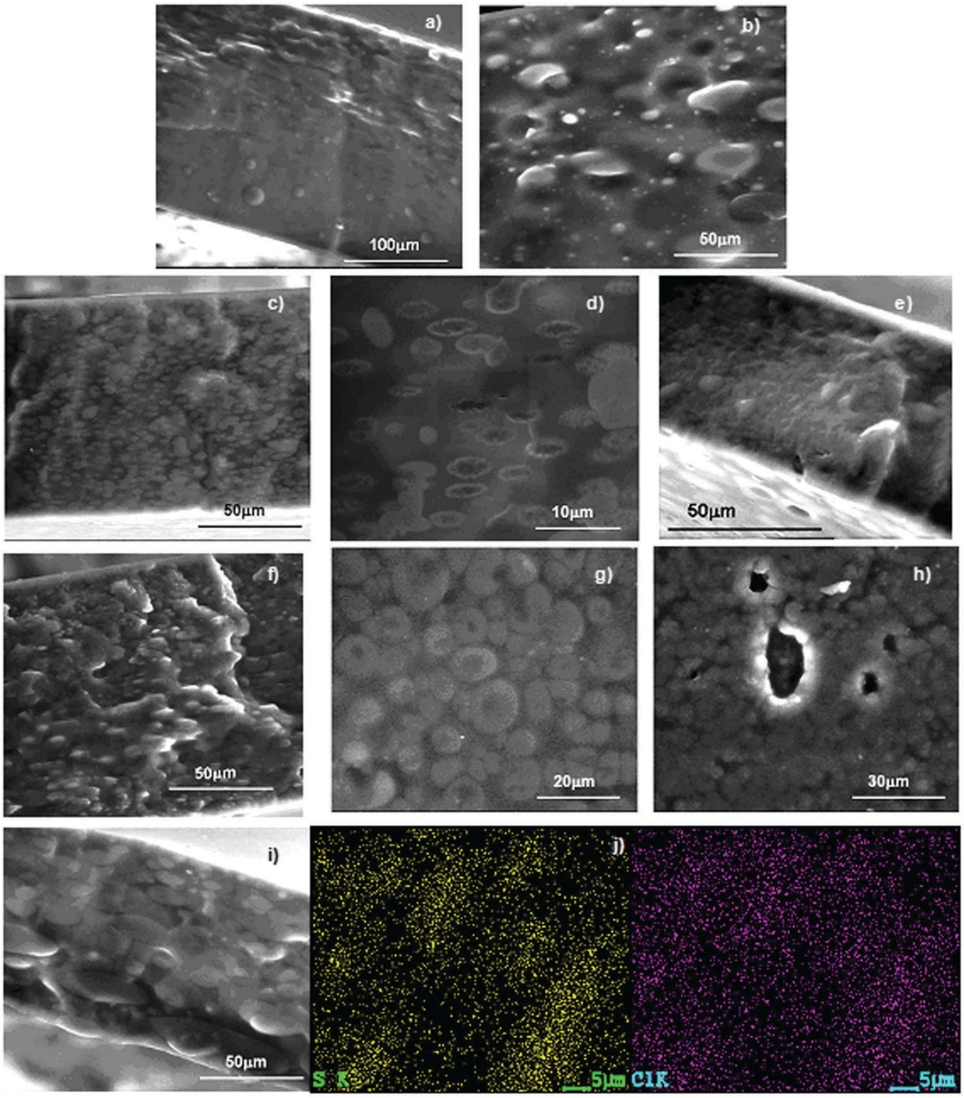


Fig. 3 SEM images of the films: (a) PDMS reference with a Pluronic surfactant; (b) cross-section of sample C-CN-25; (c and d) cross-sections of sample C-Cl-23; (e) cross-section of sample C-Cl-23P; (f) cross-section, and (g and h) surface images of sample C-CN-90; (i and j) cross-section image and EDX element mapping of sample C-Cl-100.

For the samples with chloropropylthioethyl pendant groups, the EDX analysis and mapping evidenced the presence of Cl and S in a 1/1 atomic ratio and their distribution within the samples (Fig. 3j), while for the others the presence of N was verified.

The polar domains were large enough to allow detection of the corresponding glass transition temperatures in DSC (Fig. S5, ESI†), which were higher than the T_g of the PDMS matrix. Based on SEM observations, we assume that the use of a siloxane compound as a stabilizer would be more suitable for composites with the PDMS matrix than the all-organic surfactants. Since the respective siloxane was prepared in-house, we wanted to test a more common stabilizer, which could be used on a larger scale in a more general preparation protocol. According to theoretical calculations,[39] the solubility parameter (δ) of Pluronic L81 is high (10.2 (cal cm^{-3})$^{0.5}$), despite the fact that this is a hydrophobic surfactant (HLB = 2). This value supports the observations and estimations about phase separation and thermodynamic incompatibility with PDMS and the polar silicones (Table S1, ESI†), especially those with a low dipole content (having a δ value around 8), opposite to the siloxane-based surfactant previously used, which has a δ value[17] of 8.2 (cal cm^{-3})$^{0.5}$.

Dielectric properties

After encapsulation of the polymers with very high cyano or chloro-group content into high M_n PDMS in the same proportion, the dielectric permittivities at 10 kHz were 4.7 and 4, respectively (Table 2). Similar values were observed when cyanopropyl-modified silicones were mixed with PDMS and cross-linked into inter-connected networks.[20] When comparing the materials with a lower number of polar groups, the same tendency was observed. Overall, the cyano-modified silicones had a more pronounced effect on the dielectric permittivity of the composites as compared with their chloro-containing homologues, but the

Table 2 Dielectric properties and electrical breakdown strengths of the all-silicone composites

Sample	ε' at 1 Hz	ε'	ε''	σ (S cm^{-1})	tan δ	Ebd, V μm^{-1}
		At 10 kHz				
PDMS	3.6	3.1	0.047	3.3×10^{-10}	0.015	40
C-CN-25	6.0	4.5	0.561	2.8×10^{-9}	0.123	61.5
C-CN-90	14.1	4.7	0.225	1.1×10^{-9}	0.048	63
C-Cl-23	5.4	3.9	0.289	1.4×10^{-9}	0.074	61
C-Cl-33P	5.8	3.3	0.229	1.3×10^{-9}	0.069	47
C-Cl-100	7.1	4.0	0.203	1.0×10^{-9}	0.051	40

differences were not as spectacular as in the case of neat polar silicones. This could be explained by the higher cross-linking degree of the cyano copolymers, through on-chain condensation, which limits the mobility of the dipoles. However, the dielectric permittivity values at high frequencies fit well the mixing rule applied for heterogeneous systems[1,40] without considering the effect of the surfactant and the other admixtures (see the ESI† for details and Fig. S6).

At low frequencies, which are used in certain applications, the ε' values are higher than 5.4, reaching 14.1 for C-CN-90 at 1 Hz. The increase of ε' as well as the loss of conductivity at low frequencies are assigned to Maxwell–Wagner–Sillars (MWS) polarization processes, *i.e.* to the separation of charges at interfaces with different dielectric characteristics.[41] In this case, the interfacial polarization was due to different electric properties of the polar fillers and PDMS, as well as to the presence of the surfactant.

The conductivity was one order higher at high frequencies than registered previously for the interconnected networks,[20] but remained within the limits of dielectric materials. The dielectric losses were relatively low, but again higher than those of the previous materials. We suppose that the presence of the PEO–PPO–PEO surfactant might have created this effect due to its polarity. This is sustained by the fact that a reference film based on the same PDMS polymer, but without the surfactant admixture showed lower ε', ε'' and σ values than the present work.[13] It has been reported that PEG has an important increasing effect on the dielectric permittivity of a silicone elastomer.[42]

Dielectric relaxation spectrometry (DRS) with varying temperature and frequency was further used for the samples with a high dipole content to better discern between different contributions in dielectric parameters. Since both PDMS and the polar silicones have transition temperatures below room temperature, for this experiment the temperature was modified in the range (−150)–40 °C. The evolution of dielectric constant and dielectric loss with temperature at selected frequencies (0.1 Hz, 1 Hz, 10 Hz, 10^2 Hz, 10^3 Hz, 10^4 Hz, 10^5 Hz and 10^6 Hz, respectively) provided three distinctive temperature regions (Fig. 4a and b). At low temperatures, the dielectric constant was small due to the absence of mobility of polar groups able to follow the alternative electric field. With increasing temperature, roughly around −100 °C, the polymeric chain segments gained sufficient thermal energy and their cooperative rotational motions were activated.[43] At higher temperatures, the magnitude of the dielectric constant increased considerably. The relaxations are recognized as stepwise increases in ε' curves and as peaks in ε'' curves. The primary α-relaxation processes are directly emphasized from temperature dependences of ε'' (Fig. 4c and d).

The peaks on the loss curves shifted towards higher temperatures with increasing frequency. At low frequency (0.1 Hz), sample C-Cl-100 presented three dipolar processes: the first was around −120 °C, which was assigned to α relaxation associated with the dynamic glass transition of PDMS; the second was at −80 °C, which was assigned to α relaxation of Cl-100, in agreement with the DSC glass transition temperature (Fig. S5, ESI†); and the third was at around −50 °C. The latter was observed only at lower frequencies (0.1 to 10^3 Hz) and was assigned to interfacial polarization (IFP) between the polar particles and PDMS phase.[13] At higher temperatures, the dielectric loss increased substantially due to the presence of conductivity effects. For sample C-CN-90, a peculiar behaviour was observed: the two expected α relaxations overlapped in a single broad peak centered at approximately −100 °C (0.1 Hz), while the IFP process was emphasized at around −60 °C. DSC revealed a T_g at −97 °C assigned to PDMS and another faint one at −69 °C assigned to CN-90 (Fig. S5, ESI†), which was quite different from the corresponding inter-connected network, with $T_{g(\mathrm{PDMS})}$ at −120 °C and $T_{g(\mathrm{CN\text{-}90})}$ at −63 °C.[20] Therefore, in C-CN-90, the polar filler induced a pronounced reinforcing effect, raising the T_g of PDMS by more than 20 °C. In contrast, the T_g value of the polar silicone decreased by 7 °C, compared with the neat polymer and inter-connected networks, probably as a result of a pronounced interaction with the Pluronic surfactant. These findings are in agreement with the mechanical behaviour of C-CN-90, showing the reinforcing effect of these filler particles with an impact on the piezoelectric behaviour on stretching, as will be discussed further.

The dielectric relaxation strength $\Delta\varepsilon$ of the segmental motion is associated with the magnitude of the dipole moment.[44] This parameter is defined as the difference between the dielectric constant of the polymer above and below its glass transition temperature[2] and can be used further to calculate the remanent polarization ($P_r = \Delta\varepsilon\varepsilon_0 E_p$) in the case of piezoelectric materials, as a function of poling electric field (E_p). The calculation of $\Delta\varepsilon$ was done after fitting the data to the Havriliak–Negami (HN) equation[45] (see the ESI†). The results of HN fitting of dielectric constant curves at different temperatures for samples C-CN-90 and C-Cl-100 are shown in Fig. 4(e) and (f). Data above 0 °C could be fitted and the resulting values were remarkably high, *i.e.* 32–40 for C-CN-90 and 5.1–5.5 for C-Cl-100. As will be shown further, the poling in such a case would mean applying an electric field at ambient temperature and maintaining it while cooling the composite below the fillers' glass transition. In this situation, the remanent polarization would be very high even for very low poling electric fields, on account of the high $\Delta\varepsilon$ values.

The breakdown field of the composites was measured under static conditions on films of similar thickness and the results are given in Table 2. All the samples had a dielectric strength at least equal to the PDMS reference. The composites with cyanopropyl silicones and C-Cl-23 had breakdown field values of over

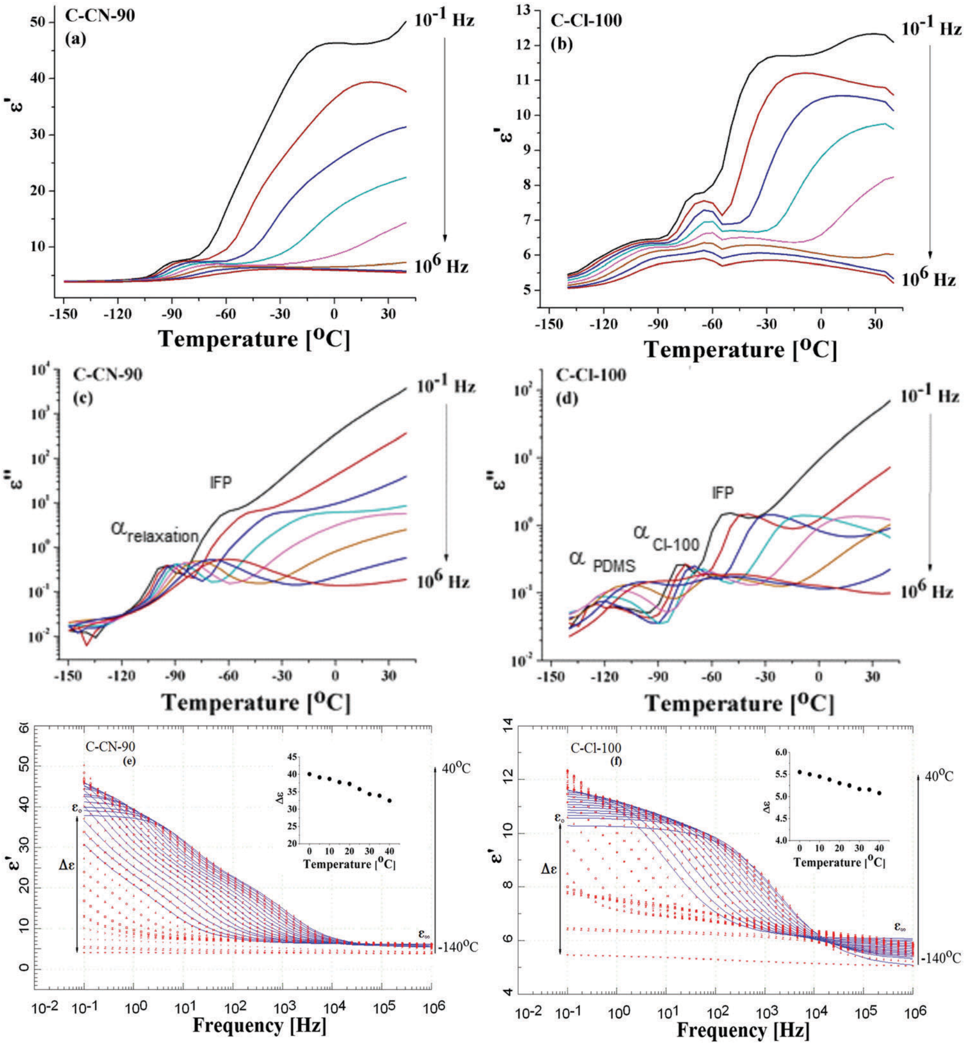


Fig. 4 The variation of dielectric constant (a and b) and dielectric loss (c and d) with temperature for C-CN-90 and C-Cl-100 samples at selected frequencies and HN – fit ((e and f) – lines); insets show the variation of dielectric relaxation strength (Δε) with temperature.

60 V μm^{-1}, which were increased by 57% in C-CN-90 compared with the reference, which is rather high for such materials containing polar fillers. The two composites with cross-linked particles with Cl groups withstood lower fields than the other composites. As discussed before, cross-linked particles might adsorb less surfactant and the excess might form separate domains, which could be responsible for lower E_{EB}. The un-bound surfactant might also be the reason for the low E_{EB} measured for the PDMS reference in this case, since a similar matrix without Pluronic surfactant withstood a higher field.[13] A decrease in E_{EB} was also reported for blends of PDMS and PEG.[42]

Mechanical properties

The stress–strain curves were registered for the all-silicone composites and the PDMS reference (Fig. 5) and the main mechanical properties (Young's modulus, maximum elongation and strength) are summarized in Table 3. At first glance, low Y values and a pronounced decrease in the maximum elongation compared with PDMS can be observed. The CN-containing composites exhibited the lowest strain, in one case under 100% (sample C-CN-90), while high strain values (reaching 760%) were registered for the composites with a moderate Cl content, either cyclics or cross-linked copolymers. It is interesting to note that a softer material was obtained with polar cyclics as the disperse phase (Y = 0.12 MPa for C-Cl-23), compared with the composites with cross-linked polymer particles (C-Cl-33P and C-Cl-100), which exhibited twice as high Y values, although these were still very soft materials. For C-Cl-100, all the mechanical parameters had lower values compared with the composites with a lower number of dipoles. The CN modified silicones acted like stiff fillers, increasing the modulus, while the Cl-modified silicones had the opposite effect. This might have been due to the different cross-linking densities within the two types of particles. In fact, various factors might have affected the mechanical properties in a complex manner, including the size of the particles, their own mechanical strength, the quality of dispersion, and so on. Again, we observed

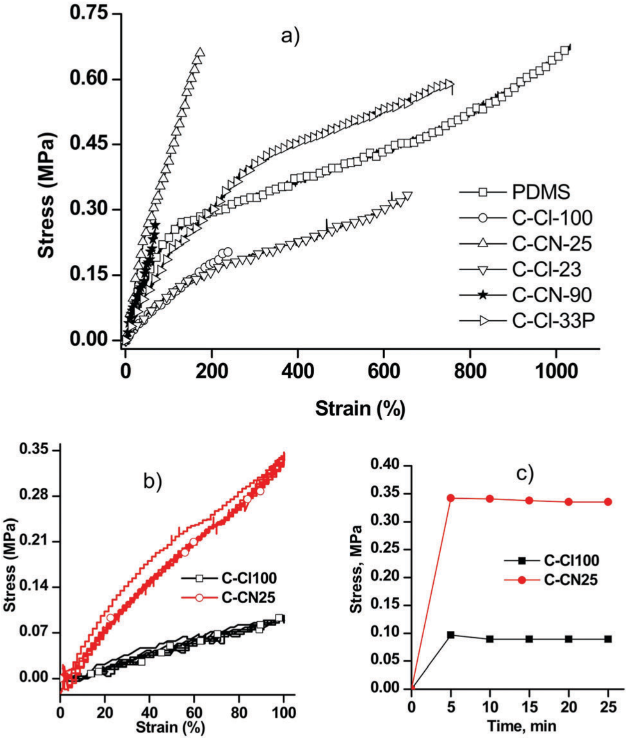


Fig. 5 Stress–strain curves of the all-silicone composites (a), cyclic tests (b) and variation of maximum stress with time (c).

Table 3 Mechanical properties of the composites

Sample	*Y* (at 10%), MPa	Elongation, %	Max strength, MPa
PDMS	0.36	1033	0.67
C-CN-25	0.48	173	0.66
C-CN-90	0.50	71	0.26
C-Cl-23	0.12	657	0.33
C-Cl-33P	0.23	759	0.57
C-Cl-100	0.21	240	0.20

the influence of the Pluronic surfactant as an immiscible admixture, comparing the mechanical properties of the PDMS references used here and in our previous work[13] both based on the same polymer. The film reported here had higher *Y* and strength, but lower maximum elongation as compared with the previous one. From Fig. 5a, stress-softening was observed for PDMS and the Cl-containing samples. This phenomenon is not characteristic for silicones,[1] but it has been observed in other cases[38,46] and it may be a drawback in terms of electromechanical stability since the materials will withstand a lower field when stretched. The fact that the PDMS reference showed this effect indicates a possible role of Pluronic surfactant in this behaviour. However, stress-softening manifested in the composites above 200% strain (and above 100% in PDMS), which was well above the best expectations for actuation.

Indeed, when fatigue resistance was tested with a maximum elongation of 100% (Fig. 5b), a small hysteresis appeared only on the first deformation due to the Mullins effect,[47] while for the next cycles the differences between stretching and relaxation were extremely small. The stress relaxation (variation of maximum stress with time during cyclic tests) (Fig. 5c) clearly showed very small modification in the stress values, which is typical for elastic materials.

Piezoelectric measurements

The piezoelectric response of samples containing the highest number of dipoles was measured using piezoelectric force microscopy (PFM). Typical PFM images consisting of surface topography, amplitude and phase of the piezoresponse are presented in Fig. 6(a) and (c) for samples C-CN-90 and C-Cl-100, respectively. A slight texture pattern can be observed in both amplitude and phase images. This demonstrates that the dipole polarization showed local variations. Under the same experimental conditions, a PDMS reference gave practically no piezoelectric response.[48]

The d_{33} coefficients measured for C-CN-90 and C-Cl-100 were 24 and 13 pm V^{-1}, respectively, on average, but reached maximum values of 47.6 and 14 pm V^{-1}. The higher longitudinal piezoelectric coefficient for C-CN-90 is in line with the higher dipole moment of cyanopropyl *versus* chloro-propyl groups[17] and is logically correlated with the high ε' value. The values measured for both samples at room temperature are in agreement with the high $\Delta\varepsilon$ values. The most known piezopolymer is PVDF, for which piezoelectric coefficients of 13–28 pm V^{-1} in bulk are considered as reference.[2] In the all-silicone composites, the measured values were in the same range, and in addition these are soft elastomers with a very low elastic modulus in the range of human skin[49] and thus their applicability could be extended to flexible or stretchable electronics, including, for example, wearable devices.

According to the literature,[2] all piezo-polymers must be polled to exhibit their piezoelectric behaviour. This operation basically means heating at a high temperature (typically around their T_g) while a high electric field is applied and maintained constant during cooling, when the dipoles are frozen in their oriented state and retain a remanent polarization (P_r). Rather few piezoelectric materials based on PDMS have been reported containing inorganic fillers, specially designed voids or high dipole organic nanoparticles.[12,46,50–52] In the present case, the observed effect was atypical, since the films were not poled in the strict sense; a low voltage was applied during PFM measurements on the cantilever. Since the polar fillers were well above their glass transition temperature, the mobility of the dipoles was high at ambient temperature. Very recently, high values of the d_{33} coefficient were measured using the same PFM technique (also without poling) for semi-interpenetrated networks with PDMS and polyimide,[48] but in that case the piezo-response was anticipated based on the known properties of polyimides. Also, the d_{33} values found in this work for all-silicone composites are similar to those reported for a silicone elastomer containing Disperse Red 1 – polymethacrylate nanoparticles,[12] after poling with 30 V μm^{-1}.

Since the all-silicone composites may withstand large strains, PFM measurements were performed on stretched samples. As can be seen in Fig. 7, the average longitudinal piezoelectric coefficient d_{33} decreased with the strain more dramatically in the case of

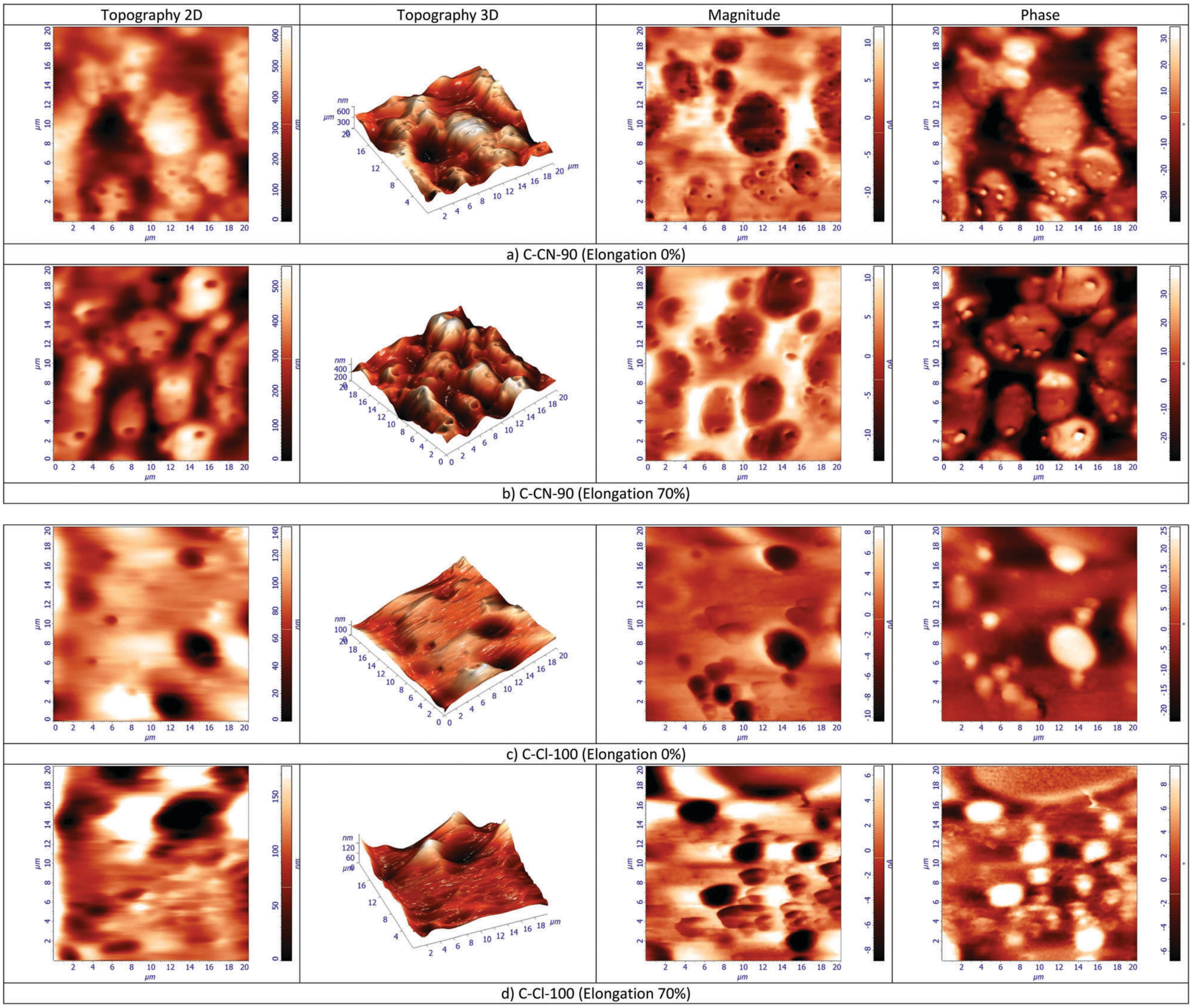


Fig. 6 PFM images showing the surface topography, amplitude and phase of the piezoresponse of C-CN-90 and C-Cl-100 samples and after stretching.

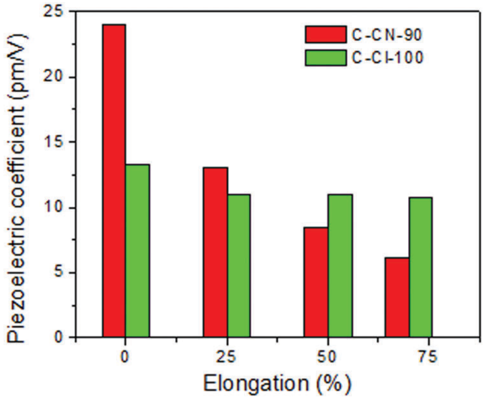


Fig. 7 Variation of piezoelectric coefficient d_{33} with elongation.

C-CN-90, which was elongated close to its limit. In contrast, C-Cl-100 behaved more robustly preserving most of its piezoelectric coefficient when strained at *ca.* 30% from its $s_{\max}$, which is very convenient for applications in stretchable/wearable devices. The decrease of the longitudinal piezoelectric coefficient can be attributed to the change in internal polarization of the material when it is subjected to elongation forces. Therefore, it is expected that the transversal piezoelectric coefficient d_{31} will increase with applied stress, indicating a possible application of the C-CN-90 composite as an energy harvester.

Another rather obvious difference is that the polar domains remained almost un-changed in C-CN-90 (Fig. 6b), but deformed in C-Cl-100 (Fig. 6d). This is an indication that the interactions of the polar particles with the matrix were more pronounced in the latter case, and is in line with the degree of cross-linking and mechanical stability of these domains. We suppose that the different behaviours of the two composites were associated with their mechanical properties. Indeed, from Fig. 5a it was observed that C-CN-90 reinforces with stretching, while C-Cl-100 softens, and this observed behaviour is in line with the thermal

Table 4 Theoretical estimation of electromechanical performance

	With ε' at 10 kHz				With ε' at 1 Hz			
Sample	$\beta/\beta_{\mathrm{ref}}$	FOM/FOM$_{\mathrm{ref}}$ (DEA)	FOM/FOM$_{\mathrm{ref}}$ (DEG)	$\Delta W/V$, mJ cm^{-3}	$\beta/\beta_{\mathrm{ref}}$	FOM/FOM$_{\mathrm{ref}}$ (DEA)	FOM/FOM$_{\mathrm{ref}}$ (DEG)	$\Delta W/V$, mJ cm^{-3}
PDMS	1.0	1.0	1.0	22.0	1.0	1.0	1.0	25.2
C-CN-25	1.1	2.6	3.4	65.8	1.3	3.0	4.0	87.3
C-CN-90	1.1	2.7	3.7	54.3	2.8	7.0	9.8	163.0
C-Cl-23	3.6	8.4	2.9	63.4	4.3	10.0	3.5	86.9
C-Cl-33P	1.6	2.3	1.5	31.8	2.4	3.3	2.1	52.5
C-Cl-100	2.2	2.2	1.3	25.7	3.4	3.3	2.0	45.8

relaxations discussed earlier. As cyano-groups are more polar than chloro-groups, their interaction with the surfactant in C-CN-90 is more pronounced, while due to on-chain cross-linking the CN-90 particles are less deformable. In the case of C-Cl-100 it seems that the surfactant acts more like a compatibilizer, ensuring better cohesion between the matrix and the filler, which is softer and thus more deformable. The decrease of d_{33} with pre-stress has been reported[12] and it can be explained based on eqn (1)[53] (where Y_{M} and Y_{D} are the Young's modulus of the matrix and filler, respectively) and taking into account the specific behaviour of the two analyzed samples.

$$d_{33} = P_{\mathrm{r}}(-1/Y_{\mathrm{M}} + 1/Y_{\mathrm{D}}). \qquad (1)$$

As discussed above, the polar domains in C-CN-90 do not elongate and this is the case of ''secondary piezoelectricity'' or ''dipole density effect''.[53] If Y_{M} decreases with elongation and Y_{D} does not change, d_{33} decreases. For C-Cl-100, deformation of the polar domains was observed, so both terms with different signs in eqn (1) change, thus they will compensate to a certain degree, and as a result the decrease of d_{33} is less pronounced. Another possible explanation for the abrupt decrease of d_{33} in C-CN-90 is percolation, which might appear and increase during stretching (since this filler is stiffer and does not follow the deformation of the matrix).[12]

In previous work, we tested polar–non-polar silicone co-networks for electromechanical response to the micromechanical impulse resulting from the free fall of steel balls onto the films sandwiched between two solid electrodes.[54] The observed effect was somehow counter-intuitive, given the composition of the materials and the absence of poling or initial electric charge. In light of the new findings, we now suppose that the observed response was due to the high piezoelectric coefficient of the cyano-modified polar silicone. The fact that d_{33} has such high values at 80–100 °C above the fillers T_{g} could indicate possible applications of these composites as charge generators at negative temperatures.

Electromechanical performance

Based on measured mechanical and dielectric properties, already established theoretical calculations[55–57] are useful for comparison and for the estimation of expected performance in actuator mode (electromechanical sensitivity β and figure of merit F_{om}(DEA)) and in generator mode (F_{om}(DEG) and maximum energy gain per cycle per unit volume), according to eqn (2)–(5).

$$\beta = \varepsilon/Y, \qquad (2)$$

$$F_{\mathrm{om}}(\mathrm{DEA}) = 3\varepsilon'\varepsilon_0 {E_{\mathrm{EB}}}^2/Y, \qquad (3)$$

$$F_{\mathrm{om}}(\mathrm{DEG}) = \varepsilon'\varepsilon_0 {E_{\mathrm{EB}}}^2/2\varphi, \qquad (4)$$

$$\frac{\Delta W_{\max}}{V} = \frac{1}{2}\varepsilon\varepsilon_0 {E_{\max}}^2\left(1 - \frac{1}{(s_{\max}+1)^2}\right), \qquad (5)$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1} is the vacuum permittivity, φ is the strain energy function of the elastomer,[55] which is assumed constant for all the materials, $E_{\max}$ is the breakdown field (E_{EB}) and $s_{\max}$ is maximum strain at break.

The calculated values, reported to the reference PDMS film, specially prepared for this study are presented in Table 4. All calculations indicate higher expected performance for the composite materials as compared with the reference. Thus, taking into account the material properties, the all-silicone composites are suitable for actuation and generation applications, both at high and low frequencies. According to electromechanical sensitivity values, the Cl containing composites have better promise in actuator mode due to their lower Young's modulus. The composites with CN polar groups seem the best materials for energy harvesting (generator mode), irrespective of the frequency, followed by C-Cl-23 on account of their breakdown field.

Conclusions

New all-silicone composite materials were prepared using a high molecular weight PDMS as the matrix and polar silicone particles as the disperse phase. These particles were stabilized with the hydrophobic commercial surfactant Pluronic L81 while the polar polymers were cross-linked within the particles in most cases. Two types of polar silicones were used for this purpose, which had either CN or Cl groups in similar proportions, attached by appropriate chemical modification reactions. The mechanical, dielectric, and piezoelectric properties were measured and discussed in correlation with morphological aspects. Soft elastomeric materials with good electric behaviour were obtained and promising electromechanical performance resulted from theoretical calculations. Our next step is the optimization of such materials, focusing on the choice of stabilization agent. We report for the first time the piezoelectric behaviour measured using PFM in all-silicone composites from amorphous components above T_{g} (at ambient temperature) without poling. Average longitudinal piezoelectric coefficients, d_{33} of 24 and 13 pm V^{-1}, comparable with those reported for PVDF were found. These values, in addition to the very low elastic modulus (mechanical properties similar to human skin) and very high dielectric relaxation strength Δε of our composites create the premises for a large range of applications, like stretchable electronics including biomedical applications (tactile sensors, acoustic transducers, and wearable devices), and low temperature employment.

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