Stretchable piezoelectric elastic composites for sensors and energy generators

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ABSTRACT

The search for a piezoelectric elastomer that generates an electrical signal when pressed and stretched has increased significantly in the last decade as they hold great promise in harvesting energy from human motion and monitoring human activities. Here, the excellent elasticity of polydimethylsiloxane-based elastomers and the piezoelectric properties of lead zirconate titanate (PZT) were combined and, using a thermally activated poling process, elastic piezoelectric composites were obtained. For this, two polydimethylsiloxane (PDMS) matrices with a molar mass of 139 kDa and 692 kDa and PZT fillers with particle sizes of 2 and 20 μm were used. For the same poling conditions, an increase in the piezoelectric response with increasing amount of filler, filler size and molar mass of the polymer matrix was observed. Overall, d33 and d31 values of 2.7–40 pC N−1 and 16–48 pC N−1 were achieved in this work with filler contents ranging from 37–72 vol%. A composite material with a PZT filler content of 38 vol% (20 μm particle size) in a commercially available PDMS with a Mw = 139 kg mol−1 exhibited high flexibility, good elasticity with long-term mechanical stretchability and high longitudinal and transverse piezoelectric coefficients of 3.6 pC N−1 and 30 pC N−1, respectively. The higher transverse piezoelectric constant d31 can be explained by an additional capacitor effect of the composite film structure. These properties are interesting features for energy conversion from human motion, monitoring human activities, and stretchable electronics. The functionality of the newly developed material is demonstrated in a pressed sensor.

1. Introduction

Piezoelectric materials have the characteristic of generating an electrical signal by an induced mechanical stress and vice versa, described by the converse and direct piezoelectric effect. They have been used in a wide range of applications such as ultrasound transducers, sensors, actuators and energy harvesters [1,2]. Piezoelectricity can be found in both organic and inorganic materials, whereas ferroelectric ceramics exhibit by far the highest response. For instance, perovskite ceramics such as barium titanate (BTO) [3,4] or lead zirconate titanate (PZT) [5,6] have a high d33 piezoelectric coefficient, high temperature stability and a high dielectric constant, which render them attractive for energy conversion materials. Below their Curie temperature Tc, BTO (Tc = 130 °C) and PZT (Tc ≥ 360 °C) feature a tetragonal or rhombohedral structure with a non-symmetric distribution of the central atom. To obtain a piezoelectric effect in a ferroelectric ceramic with randomly distributed grains, the polarization within different grains must be oriented as much as possible in the same direction. This can be achieved by subjecting the ferroelectric materials to a strong electric field via a so-called poling process, where it is assumed that the microscopic polar domains within the crystal structure are reoriented and a permanent polarization is introduced in the macroscopic sample, leading to a high...
piezoelectric response of the poled material. However, ceramics are brittle and therefore their application in flexible electronics is limited. Although more flexible alternatives such as polyed polyacryl acid [7], polyvinylidene fluoride [8,9] or disperse red 1-co-polymetlacrylate composite in polydimethylsiloxane (PDMS) [10,11] exist, their piezoelectric response is relatively weak compared to ferroelectric ceramics. To increase the piezoelectric properties of polymeric materials, often a ferroelectric powder is mixed inside a polymeric matrix such as ceramics. To increase the piezoelectric properties of polymeric materials, often a ferroelectric powder is mixed inside a polymeric matrix such as lead zirconium titanate (PZT), barium titanate or bismuth ferrite [2,12–14]. Sebastian et al. demonstrated that even flexible polymer-based composite fibers with a 60 vol% of ferroelectric fillers could be polarized by applying an electrical field up to 4 kV mm⁻¹ [15]. In order to achieve elasticity, ceramic particles can be dispersed in a elastic matrix such as PDMS, thus leading to mechanically stable materials. Such composites can undergo high deformation strain, which is an interesting feature for energy conversion from human motion, monitoring human activities and stretchable electronics [16–18]. In recent years, implantable piezoelectric biomedical devices which were powered by motions in the human body such as breath and heartbeat into electrical energy were developed which could pave the way for sustainable future health care technologies [19–21].

In this work, PZT particles of two different sizes are dispersed in two different high molecular weight PDMS matrices and the composites are poled in an electric field to enhance their respective piezoelectric properties, e.g., the d³ and d₃₁ coefficients. These two coefficients represent the ability of a material to convert a pressure applied in poling direction (d₃₃) or a tensile stress perpendicular to the poling direction (d₃₁) into electric charge, which is exploited in sensor applications. We achieved highly stretchable materials with a filler content of 37–66 vol %, which show a d₃₃ value of 2.7–40 pC N⁻¹ and d₃₁ value of 16–48 pC N⁻¹ and therefore exhibit attractive properties for sensors and energy harvesters. While the d₃₃ values of PZT/PDMS composites have been extensively reported previously and used as a basis for sensor development, the d₃₁ measurements of the corresponding composites was hardly studied, hence the potential of exploiting this feature of PZT/PDMS for energy harvesting was an integral part of this investigation [2,12,22–26]. Additionally, stability measurements were conducted to check the performance of selected composites after subjecting them to different environmental treatment such as humidity and temperature. Furthermore, we demonstrated that the longitudinal piezoelectric effect of the prepared composite materials can be utilized to construct a working prototype sensor.

2. Experimental part

2.1. Materials

2.1.1. Formulation components

PZT powders (T & P, grain size 2 and 20 µm according to the distributor) were purchased from T & Partners, Praha (PZT Division). The powder has a density of 7.6 g/cm³, a dielectric constant ε' of 2100 and piezoelectric constants d₃₃ of 450 pC N⁻¹, respectively. Sodium carbonate (Na₂CO₃) was purchased from Sigma Aldrich. Linear silanol end-functionalized polydimethylsiloxane (Mₐ = 139 kg mol⁻¹) denoted as PDMS 139 k, octamethylenetricyclooctane (D₄) and (25–35% methylhydrosiloxane)–dime-thylpolysiloxane (150 µL) in the three-roll-mill (Exakt, type 80 S) for 10 min. Thereafter, the composite was redisperssed in toluene, stirred at room temperature for approximately 2 h, treated with a 50% solution of DBTDL in toluene (112 µL). The mixture was then bath sonicated for 5 min, and then casted onto a fluorinated polymer substrate using a doctor blade. The composites were let to stand at room temperature overnight and then heated in vacuo for 7 h at 80 °C before further investigations. The composites had a film thickness of 170–250 µm (PDMS 139 k) and 120–150 µm (PDMS 692 k).

2.1.2. Hydrophobilization of PZT

To a dispersion of PZT powder (37 g) in toluene (640 mL) prepared via tip sonication (~5 min), HMDS (57 mL) was added under argon atmosphere at room temperature and stirred at 40 °C overnight. Then, the powder was recovered through centrifugation and decantation of the solvent. After a washing cycle consisting of dispersing the precipitate in toluene, the suspension was centrifuged, and the liquid was decanted again. The washing cycle was repeated thrice. The trimethylsilyl surface-modified PZT particles were kept wet for the preparation of composites.

2.1.3. Synthesis of high molecular weight linear silanol end-functionalized PDMS

D₄ was introduced in a reaction vessel equipped with mechanical stirrer and cooling mantle. Concentrated H₂SO₄ was added as a catalyst and the reaction mixture was vigorously stirred for 60 min at 25 °C, after that distilled water (2 mL) was added and the stirring was continued for another 30 min. The mixture was stored as such for 18.5 h. The polymer was dissolved in a large amount of CHCl₃ (~2.5 L), followed by repeatedly washed with an aqueous solution 5% Na₂CO₃ and warm water in order to reach a neutral pH, followed by the removal of CHCl₃ at the rotary evaporator. The polymer was further dried in a vacuum oven at 150 °C for several hours in order to remove residual cycles which were present as side products of the reaction.

The molecular weight of the polymer (Mₗ = 692 kg mol⁻¹, PDI = 5.01) was determined from gel permeation chromatography (GPC) measurements (Supporting Information SI 1).

2.1.4. PDMS composites

The trimethylsilyl surface-modified PZT powder (7–24 g) dispersed in toluene (~10 mL) by tip sonication for 2 min was mixed with PDMS 139 k or 692 k (1.5 g) and (25–35% methylhydrosiloxane)–dimethylpolysiloxane (150 µL) in the three-roll-mill for 10 min. Thereafter, the composite was redisperssed in toluene, stirred at room temperature for approximately 2 h, treated with a 50% solution of DBTDL in toluene (112 µL). The mixture was then bath sonicated for 5 min, and then casted onto a fluorinated polymer substrate using a doctor blade. The composites were let to stand at room temperature overnight and then heated in vacuo for 7 h at 80 °C before further investigations. The composites had a film thickness of 170–250 µm (PDMS 139 k) and 120–150 µm (PDMS 692 k).

2.1.5. Characterization methods

SEM images were obtained with a Nova NanoSEM 230 FEI and the investigated samples were sputtered with Au prior to the measurement. TGA was conducted with a PerkinElmer TGA7 at a heating rate of 20 °C min⁻¹ under a He gas flow. Impedance spectroscopy measurements were performed at room temperature with a Novocontrol high impedance Alpha Analyzer using a Hewlett Packard 16451 B dielectric test fixture equipped with round electrodes on circular composite samples with round sputtered gold electrodes (20 mm diameter, 20 mm thickness) on both sides. The measurements were performed in a frequency range between 0.1–10⁶ Hz. The amplitude of the probing ac electric signal applied to the samples was 1 V, and the permittivity ε' was determined from the capacitance: C = ε'ε₀A/d, where A is the electrode area and d is the thickness of the film and ε₀ is the vacuum permittivity. The permittivity values were averaged from the deviation in the film thickness of the corresponding film sample. Tensile tests were performed using a Zwick Z1010 tensile test machine with a crosshead speed of 50 mm min⁻¹. Tensile test samples, with a gauge width of 2 mm and a gauge length of 18 mm, were prepared by die-cutting. The strain was determined using a longitudinal strain extensometer. Stress versus strain curves were obtained by averaging measurements of 3–5 samples for each material. The Young’s modulus was determined from the slope of the literature [28].
the stress–strain curves at ≤10% strain. Dynamic mechanical analysis (DMA) was carried out on an RSA 3 DMA from TA Instruments. Strips of 10 mm × 20 mm from selected samples were measured under a dynamic load of 2 g, at 2% strain in the frequency range of 0.1–1 Hz at 25 °C. The mechanical loss factor tan(δ) is given as the fraction of imaginary and real storage modulus at 2% strain.

Gel permeation chromatography (GPC) measurements were done with an Agilent 1100/PSS WinGPC 8.1 system in THF (flowrate: 1 mL/min) calibrated with PDMS standards (Polymer Standards Service). The dielectric breakdown was determined using flat rigid metal electrodes with an area of 0.25 mm² embedded in an epoxy resin, which hindered electromechanical actuation of the dielectric films. Ten measurements were conducted for each sample.

2.1.6. Poling

The composite was sandwiched between two 15 mm (diameter) flexible electrodes, consisting of GNPs/CB (300/150 30 wt%) in PDMS, and two 15 mm (diameter) round aluminum electrodes. The metal electrodes were then connected to a voltage source and to the ground. Most composites were poled in an electric field of 3-18 V μm⁻¹ at 150 °C for 40 min and afterwards cooled to room temperature at a rate of 4 °C min⁻¹ with the field still switched on. This precaution was used to avoid the relaxation of the domains back to their random orientation. The field was maintained by a Stanford Research Systems PS350 high voltage device. Temperature control was ensured by a Lauda RC6 CP thermo-static oil bath connected to a closed glass container that housed the composite.

The d₃₃ piezoelectric coefficient was measured by applying a constant force (0.6 N) on the poled part of the composite, which is covered by the electrode material, that led to a voltage output. The measuring device was calibrated with a reference ceramic sample with a d₃₃ of 17.5 pC N⁻¹ in order to calculate the resulting d₃₃ coefficient. The samples measured had two conductive electrodes on them, which were applied according to a previous procedure [28].

For the d₃₃ measurements, a Zwick 2010 tensile testing machine was used to apply strain and measure the force acting on the rectangular films with dimensions of 3.5 cm × 2.5 cm (length × width). The metallic clamps of the tensile testing machine were covered with a layer of adhesive tape to insulate them from the sample. A strip of adhesive copper tape was attached to both the upper and lower clamps to make an electrical connection between the sample and the voltage readout via a current preamplifier. Both sides of the poled area of the electrets were covered with conductive electrode composites consisting of GNPs, CB and PDMS (Mₓ = 139 kg mol⁻¹) which were screen printed on both sides of the sample (Supporting information SI2). The electrodes were 11 mm in diameter. A connective strip consisting of carbon black powder, going from the poled area to the sample edge, was applied on each side of the film, facing opposite edges. After mounting the sample in the tensile testing machine, the copper tape contacted the carbon black and a Keithley 2000 recorded the current passed through a Stanford Research Systems SRS70 low noise current preamplifier while the sample was subjected to cyclic strains. Selected samples were subjected to further treatment in an oven set at 90% relative humidity (RH) at 25 °C and at 85 °C, respectively, in order to assess their performance after exposure to different environments.

3. Results and discussion

In this work, we used PZT particles with a diameter of 2 and 20 μm as a piezoelectric filler and two elastic PDMS matrices with different molar masses of 139 and 692 kDa. A schematic illustration of the preparation steps is depicted in Fig. 1, while the reaction mechanism of tin-catalyzed cross-linking of PDMS is shown in the supporting information (SI 3). SEM micrographs show that the 2 μm sized particles have a mostly homogenious size distribution, while the 20 μm particles consist of large agglomerates of primary particles (Fig. 2a and b). Size measurements conducted from the SEM micrographs concluded that the average size of those agglomerates was around 21 ± 6.5 μm similar to the size given by the supplier. Prior to the preparation of the composites, it was essential to subject the particles to surface treatment with HMDS to render them hydrophobic, thus enhancing their compatibility with the PDMS matrix [29,30]. Through the surface functionalization, the PZT particles could be dispersed more easily in toluene and did not sediment as fast as the untreated particles (Fig. 2c).

The materials prepared as described in the experimental section are named as Ex[y-z], where x represents the mass of PDMS used in kDa, y the size of the particles used in μm, and z the vol% of PZT filler. SEM micrographs of the resulting composites with different particle size and filler content are featured in Fig. 3. The effective amount of filler dispersed in the PDMS was determined from the TGA measurements where the total filler content consisted of the residual mass after burning off the PDMS polymer (Fig. 4). The vol% of PZT particles within the composites was calculated using the densities of PZT (~7.6 g/cm³), of the cross-linker (~0.98 g/cm³) and that of PDMS (~0.97 g/cm³). Under inert atmosphere, the PDMS matrix should decompose without residual mass [30]. In general, the composites tendentially feature an

![Fig. 1. Schematic illustration of the preparation of PDMS composites with PZT particles.](image-url)
enhancement in the thermal degradation stability with increasing filler content since they act as heat absorbants which is transferred to them from the polymer chains. Furthermore, the compatibilized particles also act as physical cross-linking centers for the PDMS chains through interfacial interactions which reinforce the material [31]. As a result, the temperature of maximum weight loss rate $T_{\text{max,m}}$ (m for major) of the main degradation step increased with the filler content. However, an increase of the filler content also hinders the chemical cross-linking reaction of polymers, and it was also reported that ceramics can act as catalysts, which promote the depolymerisation of PDMS at elevated temperatures [32]. Hence, $T_{\text{max,m}}$ decreased again towards lower temperatures at high filler content as observed for composites using both 2 and 20 $\mu$m PZT particles. In addition, a weak degradation step between 300 and 350 $^\circ$C noted as the temperature of maximum weight loss rate $T_{\text{max,w}}$ (w for weak) appeared for composites with filler contents above 60 vol% although it was much weaker than $T_{\text{max,m}}$ which suggests the degradation of free polymer chains due to the inhibited chemical cross-linking reaction (Table 1) [33].

The composites prepared with PDMS 139 k using 2 $\mu$m PZT exhibited higher thermal stability than the composites prepared with PDMS 692 k with regards to $T_{\text{max,m}}$, likely due to the higher chemical cross-linking density of the former due to its lower molecular weight, which limits the thermally-induced segmental movement which was also supported by the increasing filler content that contributed to more physical cross-linking centers (Fig. 4) [34]. Higher molecular weight polymer composites exhibit an increased probability of random scission of polymer chains as a result of intramolecular and intermolecular redistribution reactions which leads to depolymerisation [35]. This trend is not observed with the composites utilizing 20 $\mu$m PZT particles since their total surface area is lower and therefore does not inhibit the cross-linking reaction between the polymer chains as heavily as in the case of 2 $\mu$m PZT particles. However, the lower surface area also leads to a decrease in their ability to effectively act as physical cross-linking centers, and hence lower $T_{\text{max,m}}$ was overall observed for 20 $\mu$m PZT composites [36].

The composites exhibited an enhanced dielectric permittivity, which is attributed to the high $\varepsilon'$ of PZT ($\varepsilon' = 2'100$). The increase in $\varepsilon'$ was almost linear with increasing filler content (Fig. 5, Table 2). Here, $\varepsilon'$ seemed independent from both the particle size and the $M_w$ of the PDMS matrix. For both particle sizes of PZT used, $\varepsilon'$ values up to 34–35 were reached at a filler content of 66 vol%. The obtained $\varepsilon'$ values are in comparable range to PZT/PDMS composites reported earlier and are in good accordance to the model proposed by Yamada [5]. Although the filler content in the composites prepared in this work surpassed the percolation threshold, $\varepsilon'$ did not register an abrupt increase since, despite the high $\varepsilon'$ of the filler, PZT is not a conductive filler like metal particles which contribute to this phenomenon [37,38]. When the filler content exceeded 70 vol %, $\varepsilon'$ diminished due to the increased presence of air voids ($\varepsilon' = 1$) with higher filler content due to particle agglomeration [37]. The dielectric breakdown field, $E_B$, decreased with increasing filler content and is influenced by the PDMS matrix used, an effect which has also been observed with other elastic matrices [39]. The composites containing PDMS 692 k have a larger $E_B$ than their lower molar mass counterparts. This can be explained by the fact that the longer polymer chains can fill in the voids within the material much better than shorter polymer chains and therefore disrupt the free-electron pathway, which is induced by the application of a voltage [40]. When using 2 $\mu$m PZT particles as filler, $E_B$ decreased in a similar trend for composites using PDMS 139 k and PDMS 692 k, respectively, with the latter featuring a higher $E_B$ at comparable filler content as explained earlier. For the...
Composites using 20 μm PZT particles, the $E_b$ of the composites with PDMS 139 k was lower compared to the corresponding composites with 2 μm PZT particles, while the $E_b$ of the PDMS 692 k composites were comparable in magnitude at a filler content of ≤ 50 vol%. These observations support the argument that the particle-polymer interface layers are reduced with increasing particle size due to the reduction of the particle surface area which explains the lower $E_b$ for 20 μm PZT particles. With increasing $M_w$ of the PDMS, however, this effect diminished as seen in Fig. 5 although it declined rapidly with the filler content for the 20 μm PZT composites. The $E_b$ values exhibited large deviations due to the presence of localized defects within the material as a result of agglomerate formation through the relatively high filler content but the distribution of values narrows down after 50 vol% where the $E_b$ decreased even further as adjacent particle become more interconnected with each other.

The composites were also subjected to mechanical tensile testing (Supporting information SI 4 and 5). With increasing filler content, the strain at break values for composites PDMS 139 k decreased due to the increasing brittleness of the materials (Fig. 6, Table 3). There seemed to be no substantial difference between the smaller and larger particles in terms of the Young’s modulus $Y$ and the strain at break values manifested itself at larger filler content. By using PDMS 692 k instead of PDMS 139 k, the strain at break value was enhanced due to the higher flexibility of the polymer chains. For composites using both 2 μm and 20 μm PZT particles dispersed in both PDMS 139 k and 692 k, respectively, $Y$ increased initially with the filler content due to the reinforcing effect of the filler as additional physical cross-linking agents. As the surface-to-volume ratio was higher for the 2 μm particles, the resulting $Y$ values were higher than for the 20 μm PZT composites. However, a decrease in $Y$ at high filler contents (50 vol% or above) was observed due to the increasing aggregation of particles with rising filler content and the subsequent dewetting of the polymer at the polymer/particle interphase (Table 3, Entries 3 and 4, 6 and 7, 9 and 10, 12 and 13) [41,42]. As a result, the reinforcing effect of the particles diminished due to the reduction of the polymer/particle interactions, and hence the mechanical properties deteriorated which was manifested in both the reduction of $Y$ and the strain at break value. Below a filler content of 50%, the 20 μm PZT/PDMS composites for PDMS 692 k at filler contents showcased a higher strain at break value which indicated that the chemical cross-linking was less hindered and the polymer chains less entangled compared to the scenario where the smaller PZT particles are used as filler where the latter limits the diffusion of the polymer chains and act as physical cross-linkers.

DMA measurements performed on selected composites with roughly the similar filler content revealed a constant storage modulus, $E'$, from 0 to 1 Hz. It has to be mentioned that composites with higher filler content were not suitable for this characterization due to their increasing brittle nature. In general the storage modulus increased with the amount of filler, which is indicative of the reinforcing character of the filler thus contributing to the stiffness of the material (Fig. 7). The increase in the filler amount is associated with an increase in the particle surface area and in the resulting polymer/particle interface [43]. Hence, the loss modulus also increased since the reinforcement of PDMS with the filler required a larger force to induce the same stress. With increasing frequency, a decline in the modulus was observed, which could be due to the diminishing entanglements between the particles and the polymer chains. A steeper decline in the loss modulus, $E''$, is observed for the composites using PDMS 692 k since the cross-linking density is lower compared to the composites using PDMS 139 k, thus...
giving rise to softer and more flexible materials [44]. Both composites E139 (2–52) and E692 (20–50) are materials where the adjacent particles start to become more interconnected with each other as a result of the growing filler content. The increase in the frequency led to the separation of the interconnected particles, and hence the polymer/particle interface area increased. In the case of E139 (2–52), the increase in the polymer/particle interface led to a brief increase in both the storage modulus \( E' \) and the loss modulus \( E'' \) due to the destruction of the particle agglomerates and the ensuing activity of the resulting isolated particles as physical cross-linkers. This phenomenon was not observed for E692 (20–50) where the increase in the polymer-particle interface area was smaller due to the lower surface-to-volume ratio of the 20 \( \mu \)m PZT particles and therefore had a lower positive impact on the mechanical properties of the corresponding composites in comparison to 2 \( \mu \)m PZT particles. Therefore, the initial increase in frequency led to a decline in both \( E' \) and \( E'' \).

The goal of dispersing PZT into PDMS was to produce flexible and stretchable piezoelectric materials. However, the formed composites consist of randomly oriented dispersed ceramic particles and thus no macroscopic piezoelectric response was expected [26]. To achieve a macroscopic electromechanical response, the composites were poled at elevated temperatures and high electric fields. Previous reports showed optimized poling conditions of ferroelectric-PDMS composites at 100–150 \( ^\circ \)C and 2–7.5 \( V \mu m^{-1} \) [23, 45, 46]. As expected, under the same poling conditions (12 \( V \mu m^{-1} \) at 150 \( ^\circ \)C), an increase in the \( d_{33}^* \) piezoelectric coefficient with increasing filler content was observed. For instance, composites E139[2–z] showed an increase of \( d_{33}^* \) from 2.7 to 7.8 \( pC N^{-1} \), when the filler content increased from 37 to 52 vol\% (Table 4, Entries 1–3). It is well known for composites that elevated temperature and higher electric field results in a higher piezoelectric constant (due to a higher mobility of dipole movement of the ferroelectric filler), on the other hand the maximum temperature is limited by the melting point and decomposition temperature of the polymer. Furthermore, the maximum allowed electric field (\( E_R \)) is determined by the dielectric strength of the material (\( E_b \)), where \( E < E_b \), and further decreases with increasing temperature. Therefore, some of the different

![TGA curves of PDMS/PZT nanocomposites with different filler content: average particle size of PZT is 2 \( \mu \)m and PDMS 139 k (a) and PDMS 692 k (b) and average particle size of PZT is 20 \( \mu \)m and PDMS 139 k (c) and PDMS 692 k (d), respectively.](image)

**Table 1**

| Sample     | PZT [vol\%] | PDMS \( M_w \) [kg\cdot mol\(^{-1}\)] | \( T_{max,w} \) (\(^\circ \)C) | \( T_{max,m} \) (\(^\circ \)C) |
|------------|-------------|---------------------------------------|-----------------------------|-----------------------------|
| E139 (2–37)| 37.4        | 139                                   | –                           | 560                         |
| E139 (2–40)| 39.6        | 139                                   | –                           | 667                         |
| E139 (2–52)| 51.8        | 139                                   | 350                         | 650                         |
| E139 (2–67)| 66.5        | 139                                   | –                           | 476                         |
| E692 (2–45)| 44.7        | 692                                   | –                           | 564                         |
| E692 (2–55)| 54.6        | 692                                   | 355                         | 534                         |
| E692 (2–72)| 72.4        | 692                                   | –                           | 516                         |
| E139 (20–38)| 38         | 139                                   | –                           | 543                         |
| E139 (20–47)| 46.5       | 139                                   | 364                         | 516                         |
| E139 (20–66)| 66.2       | 139                                   | –                           | 550                         |
| E692 (20–43)| 43         | 692                                   | –                           | 559                         |
| E692 (20–49)| 48.7       | 692                                   | –                           | 559                         |
| E692 (20–50)| 50.3       | 692                                   | –                           | 529                         |
| E692 (20–61)| 60.7       | 692                                   | 305                         | 524                         |

![Fig. 4. TGA curves of PDMS/PZT nanocomposites with different filler content: average particle size of PZT is 2 \( \mu \)m and PDMS 139 k (a) and PDMS 692 k (b) and average particle size of PZT is 20 \( \mu \)m and PDMS 139 k (c) and PDMS 692 k (d), respectively.](image)
Composites were polarized using different conditions. The breakdown field, $E_B$, is reduced with increasing filler content due to particle agglomeration as explained earlier. Since the $E_B$ of the composite E139 (2–67) was at 13 V μm$^{-1}$, poling at 12 V μm$^{-1}$ was quite risky in terms of inducing dielectric breakdown. Therefore, E139 (2–67) was poled at 6 V μm$^{-1}$ at a temperature of 155 °C instead. As a result, this composite exhibited a $d_{33}$ of 22.7 pC N$^{-1}$ (Fig. 8, Table 4, Entry 5). Increasing the molecular weight of the PDMS matrix allowed the incorporation of more filler, while the dielectric breakdown field was enhanced. Therefore, a composite E692 (2–72) could be prepared and poled at 12 V μm$^{-1}$. However, it was difficult to remove it from the electrodes after poling at 150 °C since it easily broke apart during the removal because of its brittleness. To overcome this problem, the poling temperature was reduced to 100 °C, which enabled a facile removal of the sample from the electrodes after poling. The piezoelectric response of this poled composite was $d_{33} = 30$ pC N$^{-1}$. With this composite, it has also been illustrated that the poling temperature increased the $d_{33}$ of the resulting composite, which is in agreement with the literature [47]. For instance, when E692 (2–72) was poled at an electric poling field of 12 V μm$^{-1}$ and the temperature was increased from 24 °C to 159 °C, the $d_{33}$ coefficients increased from 20.5 to 30 pC N$^{-1}$ (Table 4, Fig. 8, Entries 10 and 11).

Aside from the poling temperature, the electric field with which the composites are poled also has an impact on the $d_{33}$. The increase in the electric field leads to an enhancement in the $d_{33}$ as shown by E139 (2–67) where an increase of the $d_{33}$ from 15.8 to 22.7 pC N$^{-1}$ was observed when the electric field was increased from 3 to 6 V μm$^{-1}$ at 155 °C–159 °C (Table 4, Entries 4 and 5). In direct comparison, E139 (20–66) with larger particles exhibited a $d_{33} = 40$ pC N$^{-1}$ when poled at

**Fig. 5.** Permittivity $\varepsilon'$ and breakdown field $E_B$ of PZT/PDMS nanocomposites with an average particle size of 2 and 20 μm in PDMS 139 k and 692 k matrices.

**Table 2** Summary of dielectric permittivity at $10^5$ Hz and dielectric breakdown field of PDMS/PZT nanocomposites with PZT with an average particle size of 2 μm and 20 μm.

| Sample     | PZT [vol%] | PDMS $M_w$ [kg·mol$^{-1}$] | Permittivity $\varepsilon'$ @ $10^5$ Hz | $E_B$ [V μm$^{-1}$] |
|------------|------------|-----------------------------|----------------------------------------|---------------------|
| E139 (2–37)| 37.4       | 139                         | 14 ± 0.2                               | 39 ± 10             |
| E139 (2–40)| 39.6       | 139                         | 20 ± 0.3                               | 33 ± 12             |
| E139 (2–52)| 51.8       | 139                         | 27 ± 0.7                               | 21 ± 6              |
| E139 (2–67)| 66.5       | 139                         | 34 ± 3.4                               | 13 ± 3              |
| E692 (2–45)| 44.7       | 692                         | 14 ± 0.3                               | 44 ± 9              |
| E692 (2–55)| 54.6       | 692                         | 29 ± 0.2                               | 37 ± 8              |
| E692 (2–72)| 72.4       | 692                         | 25 ± 1.7                               | 29 ± 3              |
| E139 (20–38)| 38        | 139                         | 16 ± 0.2                               | 26 ± 8              |
| E139 (20–47)| 46.5      | 139                         | 25 ± 0.2                               | 25 ± 5              |
| E139 (20–66)| 66.2      | 139                         | 35 ± 1.5                               | 22 ± 2              |
| E692 (20–43)| 43        | 692                         | 21 ± 0.1                               | 46 ± 12             |
| E692 (20–49)| 48.7      | 692                         | 25 ± 0.2                               | 46 ± 8              |
| E692 (20–50)| 50.3      | 692                         | 30 ± 0.5                               | 40 ± 11             |
| E692(20–61)| 60.7      | 692                         | 33 ± 1.3                               | 19 ± 4              |

**Table 3** Summary of the mechanical properties of PDMS/PZT nanocomposites.

| Sample     | PZT [vol%] | PDMS $M_w$ [kg·mol$^{-1}$] | $Y_{CM}$ [MPa] | Maximum strain @ break [%] |
|------------|------------|-----------------------------|----------------|-----------------------------|
| E139 (2–37)| 37.4       | 139                         | 3.9 ± 0.9      | 307 ± 82                    |
| E139 (2–40)| 39.6       | 139                         | 5.3 ± 0.6      | 302 ± 46                    |
| E139 (2–52)| 51.8       | 139                         | 11 ± 1.9       | 51 ± 19                     |
| E139 (2–67)| 66.5       | 139                         | 8 ± 1.4        | 5.9 ± 1.2                   |
| E692 (2–45)| 44.7       | 692                         | 4.8 ± 0.9      | 249 ± 81                    |
| E692 (2–55)| 54.6       | 692                         | 6.9 ± 1.7      | 100 ± 87                    |
| E692 (2–72)| 72.4       | 692                         | 2.0 ± 0.1      | 28 ± 0.8                    |
| E139 (20–38)| 38        | 139                         | 4.3 ± 0.2      | 254 ± 136                   |
| E139 (20–47)| 46.5      | 139                         | 7.9 ± 0.9      | 273 ± 108                   |
| E139 (20–66)| 66.2      | 139                         | 3.2 ± 0.5      | 27 ± 16                     |
| E692 (20–43)| 43        | 692                         | 4.5 ± 1.3      | 683 ± 93                    |
| E692 (20–49)| 48.7      | 692                         | 6.9 ± 0.9      | 727 ± 67                    |
| E692 (20–50)| 50.3      | 692                         | 5.2 ± 0.3      | 209 ± 115                   |
| E692(20–61)| 60.7      | 692                         | 2.7 ± 0.2      | 12 ± 3.2                    |

**Fig. 6.** Young’s modulus $Y$ and strain-at-break values of composites consisting of 2 μm (left) and 20 μm (right) PZT particles using PDMS 139 k (filled symbols) or 692 k (empty symbols) as polymer matrix.
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Summary of Fig. 7. DMA graphs showing the storage modulus $E'$, loss modulus $E''$ and loss factor $\tan \delta$ of selected PZT/PDMS composite materials containing roughly the same filler content with varying filler size and molecular weight of the PDMS matrix.

![DMA graphs showing the storage modulus $E'$, loss modulus $E''$ and loss factor $\tan \delta$ of selected PZT/PDMS composite materials containing roughly the same filler content with varying filler size and molecular weight of the PDMS matrix.](image)

Table 4

| Entry | Sample | PDMS $M_w$ [kg·mol⁻¹] | PZT [vol%] | Poling $T$ [°C] | Poling field [V/µm] | $d_{33}^*$ [pC·N⁻¹] | $d_{31}^*$ @25% strain [pC·N⁻¹] |
|-------|--------|------------------------|------------|-----------------|----------------------|---------------------|-------------------------------|
| 1     | E139 (2-37) | 139                    | 37.4       | 159             | 12                   | 2.7                 | 16                            |
| 2     | E139 (2-40) | 139                    | 39.6       | 155             | 12                   | 3.5                 | 26                            |
| 3     | E139 (2-52) | 139                    | 51.8       | 150             | 12                   | 7.8                 | –                             |
| 4     | E139 (2-67) | 139                    | 66.5       | 159             | 3                    | 15.8                | –                             |
| 5     | E139 (2-67) | 139                    | 66.5       | 155             | 6                    | 22.7                | –                             |
| 6     | E139 (2-67) | 139                    | 66.5       | 109             | 6                    | 20                  | –                             |
| 7     | E692 (2-55) | 692                    | 54.6       | 159             | 12                   | 13.5                | –                             |
| 8     | E692 (2-55) | 692                    | 54.6       | 153             | 18                   | 14                  | –                             |
| 9     | E692 (2-55) | 692                    | 54.6       | 99              | 12                   | 16.1                | –                             |
| 10    | E692 (2-67) | 692                    | 72.4       | 159             | 12                   | 30                  | –                             |
| 11    | E692 (2-67) | 692                    | 72.4       | 23.6            | 12                   | 20.5                | –                             |
| 12    | E139 (2-38) | 139                    | 38         | 145             | 12                   | 3.6                 | 30                            |
| 13    | E139 (2-47) | 139                    | 46.5       | 25              | 12                   | 7.8                 | –                             |
| 14    | E139 (2-47) | 139                    | 46.5       | 151             | 12                   | 9                   | –                             |
| 15    | E139 (2-47) | 139                    | 46.5       | 151             | 12                   | 7.2                 | –                             |
| 16    | E139 (2-47) | 139                    | 46.5       | 149             | 18                   | 6                   | –                             |
| 17    | E139 (2-66) | 139                    | 66.2       | 25              | 12                   | 33                  | –                             |
| 18    | E139 (2-66) | 139                    | 66.2       | 101             | 6                    | 35                  | –                             |
| 19    | E139 (2-66) | 139                    | 66.2       | 101             | 12                   | 35                  | –                             |
| 20    | E139 (2-66) | 139                    | 66.2       | 159             | 12                   | 40                  | –                             |
| 21    | E139 (2-66) | 139                    | 66.2       | 25              | 12                   | 34                  | –                             |
| 22    | E692 (2-43) | 692                    | 43         | 149             | 12                   | 6.8                 | 48                            |
| 23    | E692 (2-49) | 692                    | 48.7       | 150             | 12                   | 7.8                 | –                             |
| 24    | E692 (2-50) | 692                    | 50.3       | 104             | 12                   | 13                  | –                             |
| 25    | E692 (2-61) | 692                    | 60.7       | 25              | 12                   | 23                  | –                             |
| 26    | E692 (2-61) | 692                    | 60.7       | 100             | 6                    | 27                  | –                             |

* Electrodes where screen printed on two opposite surfaces prior to poling.

159 °C and 12 V µm⁻¹ (Fig. 8, Table 4). This is in line with previous reports which stated that the $d_{33}^*$ increases with the particle size in PZT composites [25,46].

In comparison to the permittivity $\varepsilon^*$ which featured a linear increase with filler content, $d_{33}^*$ values were quite small until 30 vol% which corresponds to the percolation threshold for isotropically dispersed particles [37]. Therefore, $d_{33}^*$ exhibited a significant increase above the percolation threshold as the composites experience a transition from a 0–3 to 1–3 composite where adjacent particles became interconnected (Fig. 3) [5]. The 20 µm PZT composites showcased higher $d_{33}^*$ since there are less polymer/particle multilayers along the film thickness due to the larger particle size, therefore stress is more effectively transferred between the PZT domains.

Apart from $d_{33}^*$, the $d_{31}^*$ piezoelectric coefficient was also measured in this study. The force acting on the composites during the $d_{33}^*$ measurements is parallel to the electric field applied during poling, while the applied force during the $d_{31}^*$ measurement is perpendicular to the poling direction. The experimental setup for the $d_{31}^*$ measurement was described in a previous report by Ko et al. (Supporting Information SI 6) [11]. Similar to the $d_{33}^*$, the $d_{31}^*$ piezoelectric coefficient of composites with similar filler content, poling conditions and identical strains increased with the PZT particle size. The difference in the performance of the two composites E139 (2–37) and E139 (20–38) can be seen in the generated charges and voltages (Fig. 9). The cyclic strain measurements conducted for the composites using the 2 µm at 25% strain and at a frequency of 0.1 Hz led to an output of 1.58 V or 0.9 nC which corresponded to a $d_{31}^*$ of 16 pC N⁻¹ (Fig. 9a-c) with a tensile force of 2.9 N acting on the E139 (2–37). When E139 (20–38) was subjected to the same measurements, the voltage generated from the cyclic measurements at the same strain and frequency increased from 1.58 V to 2.3 V, with the latter voltage corresponding to generated charges of 1.25 nC and a $d_{31}^*$ value of 30 pC N⁻¹, as a result of increasing the PZT particle size from 2 to 20 µm. The corresponding tensile force to strain E139 (20–38) was 3.02 N. The larger output exhibited by the composites with 20 µm PZT particles composed of agglomerates of primary PZT particles is attributed to the higher connectivity between the particles due to the shorter interparticle distance [48]. The reduced interface area between the particle and the polymer associated with the
increase in the size of the particle leads to less imperfections in the joining the particles [49]. In short, different stresses act on the PZT particles depending on their size, and in the case of 20 μm PZT particles the shorter interparticle distance between the primary particles within the agglomerates lead to a higher stress at the contact point between particles [17,18]. Hence, the positive correlation between stress and piezoelectric properties is reflected in the higher $d_{33}^*$ and $d_{31}^*$ values for the composites using the 20 μm PZT particles.

The long-term reliability of the films were confirmed since the generated charges remained within the similar regime when assessing the performance at different time intervals (Fig. 9a and d). Furthermore, composites containing 20 μm PZT particles dispersed in PDMS 692 k were also subjected to $d_{31}^*$ measurements at similar filler content (43 vol%) in order to determine the effect of the polymer matrix (Fig. 10). Due to the increase in structural defects with increasing filler content caused by particle agglomeration, composites with filler content above 50 vol% could not be investigated for the performed $d_{31}^*$ measurements.

For the synthesis of E692 (20–43) more toluene had to be used, hence the formulated films were thinner than the composites with PDMS 139 k using the same amounts of reagents. The presence of defects in the PDMS 692 k composites could lead to a higher rupture probability, therefore the films were initially stretched to 15% strain, which yielded a $d_{31}^*$ of $\sim 40 \text{ pC N}^{-1}$ from an output voltage of 1.96 V (Fig. 10a and c) and a charge of 0.91 nC at a force of 1.23 N. When the film was stretched to 25%, the generated $d_{31}^*$ surpassed 40 pC N$^{-1}$ and the output voltage of 3.08 V, the charge of 2.11 nC at a force of 1.87 N was obtained. Unfortunately, the film experienced rupture after a few days of measurement (Fig. 10b and d). As shown earlier the PDMS 692 k matrix reduced the Young’s modulus of the composite materials compared to PDMS 139 k matrix, which should lead to an increase of output current and hence also a larger $d_{31}^*$ coefficient since a higher stress acts between adjacent particles due to the more efficient stress transfer to the particles from the external source [18]. As can be seen from the measurement the $d_{31}^*$ coefficient increased from 30 to 48 pC N$^{-1}$ by changing the matrix from PDMS 139 k to PDMS 692 k. This renders it more beneficial for applications because higher output currents can be generated, or less input force is needed. The results obtained for the $d_{31}^*$ are higher as compared to $d_{33}^*$, which is usually not the case. We assume that the capacitor effect related to the change in charge densities of the composites plays a major role. Furthermore, the force to generate the desired strains are higher than the strains to which the composites were subjected to during the $d_{33}^*$ measurements. During cycling the thickness of the composite films will change, which affects the interparticle distance as mentioned earlier since they were incorporated within the composites alone.

Fig. 8. Longitudinal piezoelectric coefficient $d_{33}^*$ of various composites containing PZT with a particle size of 2 μm (left) and a particle size of 20 μm (right), poled at different conditions. Non-poled reference samples using PDMS 139 k (square) and 692 k (star) are illustrated in red color.

Fig. 9. The $d_{31}^*$ and charges generated by E139 (2–37) at a strain of 25%, the generated charges and voltage from 5 cycles when the sample was strained by 25% at 0.1 Hz, 88 days after poling (top row) and $d_{31}^*$ and charges generated by E139 (20–38) at a strain of 25% and the generated charges and voltage from 6 cycles when the sample was strained by 25% at 0.1 Hz, 10 days or 225 h after poling (bottom row).
through physical cross-linking. Hence, a difference in the charge density will occur.

Although the generated voltages are comparable to the output of other PZT composites, the higher strains which can be generated with the composites featured in this work expand their potential as dielectric elastomers used to generate electricity [50,51].

The effect of the environment on the material performance was also investigated for selected composites. After exposure to 90% relative humidity (RH) for 24 h, the $d_{31}$ of E139 (2–40), at a strain of 25%, was altered from 30 to 36 pC N$^{-1}$, which corresponded to a change in the charge from 1.92 nC to 1.8 nC. The material softened after this treatment, therefore the $d_{31}$ increased despite the reduction in the generated charge. The exposure of E139 (2–37) to 80$^\circ$C for the same period of time saw the $d_{31}$ slightly change from 18.2 to 20.5 pC N$^{-1}$ and a change in the charge from 0.97 nC to 1.09 nC (Fig. 11). Thus, it has been found that such composites have not shown any major changes in their piezoelectric $d_{31}$ coefficients especially at enhanced temperatures below $T_c$ thus indicating their ability to be used under those selected environmental conditions.

Composite E139 (20–38) generated a voltage of 2.3 V when stretched by 25% and has been found to exhibit the best compromise between piezoelectric performance and mechanical flexibility and stability. To demonstrate the potential of the newly developed material for applications, a demonstrator consisting of a clamping/contact device and a measuring device with LCD display was constructed (Fig. 12). The piezoelectric film sensor is clamped in the contact device and contacted via two circuit boards on the front and back, which connect the sensor to the measuring device via cables. The sensor signal is amplified and filtered in the measuring device using a "voltage mode amplifier". Then the signal is digitized with the ADC. The first line from the LCD shows the signal curve and in the second line the current peak value is recorded for a few seconds. The average offset voltage of the measuring circuit has already been subtracted from the peak value. Only the positive signal deflection is taken into account in the measurement. With the voltage amplitude, the signal influence by the deformation of the piezo film can be compared and assessed. In the present device, the piezo film signal is loaded with 500 k$\Omega$ and then amplified with 20 V. The measured value full scale (0023) corresponds to an amplitude of about 165 mV of the piezo film. For example, a displayed value of 100 corresponds to a voltage of 16 mV on the piezo with a load of 500 k$\Omega$. Fig. 12 shows how the mechanical stress induced by pressing a plastic knob by a finger generates an electrical signal, which is detected by the black electronic device.

4. Conclusions

Flexible PZT/PDMS composite films with a thickness of 120–250 μm were prepared, starting from two PDMS matrices of different molar mass and surface functionalized PZT particles of 2 μm and 20 μm. Elastic composites with a large content of filler were successfully prepared by the doctor blading technique. They were poled in a strong electric field at elevated temperature in order to induce a remanent polarization of the ferroelectric particles responsible for the macroscopic piezoelectric response. The poled composites containing 20 μm particles produced larger piezoelectric response coefficients (both $d_{31}$ and $d_{33}$) than the composites using 2 μm PZT particles at similar filler content. The potential of the most promising composite in a press sensor was demonstrated. Because of the good elastic and piezoelectric properties these materials are highly attractive for applications in sensing, energy harvesting, and stretchable electronics.

CRediT authorship contribution statement

**Jose Enrico Q. Quinsaat**: Investigation, Methodology, Formal analysis, Writing - original draft. **Tym de Wild**: Formal analysis, Writing - review & editing. **Frank A. Nüesch**: Funding acquisition, Supervision,
Fig. 11. Generated charges of E139 (2–40)(a,b) and E139 (2–37)(c,d) before and after humidity and thermal treatment, respectively.

Fig. 12. The components used for the construction of press sensor (a), photograph of the piezoelectric film with black conductive films on top and bottom (b), schematic representation of the press sensor in the relaxed (c) and press state (d) as well as the photograph of the sensor and the electronic device used to monitor the generated electrical signal. A change in the Sig Peak from 0 to 0.023 can be seen for the relaxed (e) and pressed sensor (f).
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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