Robust Three-Component Elastomer–Particle–Fiber Composites with Tunable Properties for Soft Robotics

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Materials with tunable properties, especially dynamically tunable stiffness, have been of great interest for the field of soft robotics. Herein, a novel design concept of robust three-component elastomer–particle–fiber composite system with tunable mechanical stiffness and electrical conductivity is introduced. These smart materials are capable of changing their mechanical stiffness rapidly and reversibly when powered with electrical current. One implementation of the composite system demonstrated here is composed of a polydimethylsiloxane (PDMS) matrix, Field’s metal (FM) particles, and nickel-coated carbon fibers (NCCF). It is demonstrated that the mechanical stiffness and the electrical conductivity of the composite are highly tunable and dependent on the volume fraction of the three components and the temperature, and can be reasonably estimated using effective medium theory. Due to its superior electrical conductivity, joule heating can be used as the activation mechanism to realize \( \approx 20 \times \) mechanical stiffness changes in seconds. The performance of the composites is thermally and mechanically robust. The shape memory effect of these composites is also demonstrated. The combination of tunable mechanical and electrical properties makes these composites promising candidates for sensing and actuation applications for soft robotics.

The ability to tune the mechanical stiffness between a soft state and a rigid state is essential for various living systems to navigate nature. Examples for this range from muscle-powered motor tasks and sexual reproduction, to spontaneous change in shape for predator evasion.\(^\text{[1]}\) Similar to their natural counterparts, engineered materials with tunable properties including mechanical stiffness have the potential to be used in a broad range of engineering applications.\(^\text{[1,2]}\) Structures made with these materials can change their mechanical rigidity in static or dynamic systems to extend their workspace.\(^\text{[1–4]}\)

Multiple strategies have been pursued recently to achieve stiffness tunability, including pneumatic jamming,\(^\text{[3,5,6]}\) chemical interactions,\(^\text{[7]}\) opposing actuator structures,\(^\text{[8–10]}\) magnetorheological fluids,\(^\text{[11,12]}\) external/internal heating of materials with phase change\(^\text{[13–24]}\) or glass transition,\(^\text{[25–28]}\) or through combinations of these techniques.\(^\text{[13,29]}\) Among phase-changing materials, low melting point alloys (LMPA) have been used widely as they are highly electrically conductive, rigid as metal at room temperature, and their melting point can be as low as 47.2 °C\(^\text{[21]}\) or 62.0 °C.\(^\text{[20]}\) LMPA layers, channels, foams, lattices, and particles have been incorporated as fillers into soft elastomers and shape memory polymers to create engineering materials with stiffness tunability.\(^\text{[13,17,18,20–23]}\) In addition to tuning mechanical stiffness, LMPA fillers can also enhance the thermal and electrical properties of the composites.\(^\text{[18,30,31]}\) Another example of smart composites with tunable stiffness containing phase-changing components is conductive propylene-based elastomers (CPBE),\(^\text{[24]}\) which have a propylene–ethylene copolymer elastomer matrix and dispersed...
structured carbon black particulates for electrical conductivity. These smart composites can soften when activated through Joule heating or external heating above 75 °C, the melting point of the copolymer matrix. Stiffness tunability is also closely related to shape memory effect in materials. Many of the recently engineered smart materials with tunable stiffness exhibit shape memory effect. Shape memory has the ability of a material to be programmed into a new temporary shape and then recover to its initial shape upon being triggered by external stimuli. Shape memory has been achieved before in polymers by incorporating liquid-crystal elastomers, semi-crystalline elastomers, percolating networks of cellular nanofibers, stearic acid, and supercooled salt solution. Smart materials with tunable stiffness have been used as actuation mechanisms for soft grippers based on mechanical interlocking or dynamically tunable dry adhesion for soft crawling robots, for minimal invasive continuum devices, and for reconfigurable surfaces in drones. However, the existing smart materials still exhibit limited tunability of mechanical stiffness and/or electrical/thermal conductivity (either too high or too low), and poor mechanical robustness for repeated use, thus presenting challenges in terms of activation voltage (too high) and activation time (too long) for their applications in soft and reconfigurable robotics. These limitations can be attributed to the fact that most of the existing smart composites are composed of one matrix component and one functional component with low aspect ratio. For example, high electrical conductivity requires percolation, which is difficult to achieve with merely particle inclusions in an elastomeric matrix.

Here, we introduce a novel three-component elastomer–particle–fiber composite system containing LMPA particles and conductive fibers, to overcome the limitations of existing two-component smart materials with tunable stiffness (Figure 1). Our composite system is featured with high tunability of electrical/thermal conductivity due to the presence of the third phase of conductive fibers, and tunable mechanical stiffness due to the phase of LMPA particles. We implement the composite system using a polydimethylsiloxane (PDMS) host matrix, Field’s metal particles, and nickel-coated carbon fibers (NCCF). FM is a eutectic alloy of bismuth, indium, and tin with a low melting point at 62.0 °C. As FM particles are rigid at room temperature with a Young’s modulus of 9.25 GPa, the composites are expected to be relatively rigid at room temperature. In addition, both PDMS and NCCF are stable up to 220 °C. The FM particles and NCCF can be homogeneously dispersed in the elastomer matrix. Thus, the composite can be thermally and mechanically robust for repeated use.

The conceptual design, experimental implementation, and sample demonstration for the electrically conductive stiffness tunable composites are shown in Figure 1. The topological difference in the microstructure of a two-component elastomer–particle composite and a three-component elastomer–particle–fiber composite is shown in Figure 1a. When only spherical particles made of FM are present in the elastomer matrix, it is hard to form a percolation network for the composite to be electrically conductive. However, when both the FM particles and the conductive NCCF are included, it is much easier to form. The electrical conductivity of the elastomer–particle–fiber composite can thus be tuned easily by varying the volume fraction of the three components. The three-component composites were fabricated using a multi-step pestle-and-mortar method for mixing and subsequent casting and curing. For comparison purpose, we also fabricated two-component PDMS–FM particle composites.

Scanning electron microscopy (SEM) images of the cross-sectional cuts of these composites qualitatively verify the expected microstructure difference, as shown in Figure 1b. Here the PDMS–FM composite is not electrically conductive, but the PDMS–FM–NCCF composite can be highly conductive. It can be clearly seen that the NCCF bridge between the FM particles to create conductive pathways (right panel in Figure 1b). Figure 1c shows that a thin strip of the three-component smart composite can hold a 20 g weight in the cantilever beam configuration with a small displacement at the tip of the beam. Upon demand, certain portion of the beam can be selectively activated with direct Joule-heating using a portable power supply, e.g., lithium ion polymer batteries. When the temperature of the smart composite is elevated above 62.0 °C, the FM particles will melt into droplets and the mechanical stiffness of the composite will decrease sharply such that the beam deflection...
increases dramatically. Videos S1, S2, and S3 in the Supporting Information show this selective activation of portion of the smart material from rigid to soft through Joule heating with input power rates of 1.18 W (1.25 V by 0.94 A), 10.0 W (4.0 V by 2.5 A), and 17.0 W (3.4 V by 5.0 A), respectively. In particular, the smart composite sample in Video S2, Supporting Information, has been activated and deactivated more than 50 cycles without degradation of its performance, evidencing both mechanical and thermal robustness of these smart materials.

We systematically characterized the stiffness of these smart composites using both experiments and effective medium approximation (EMA). The Young’s moduli of the composites are estimated from stress–strain curves obtained in tensile testing. Results show that the composites can withstand \(\approx6\%\) strain in the rigid state, and \(\approx20\%\) strain in the soft state before failure (Figure S1, Supporting Information), comparable to that of previously reported LMPA-based composites.[20] The EMA efforts are based on the semi-empirical Halpin–Tsai model.[52,53] In the first step of the modeling, the effective elastic modulus of the PDMS–FM composite is calculated from Halpin–Tsai model considering the FM particles as fillers into the PDMS host matrix (Equation (1)–(4), Supporting Information). Then this effective elastic modulus is used as the elastic modulus of a composite host matrix in the second step, where the effective elastic modulus of the liquid particles of FM is considered to be negligible. See the Supporting Information for more details about this procedure.

Figure 2a compares the elastic moduli of the PDMS–FM–NCCF and PDMS–FM composites in the rigid and soft states, along with the elastic moduli of two PDMS–NCCF composites. In general, the experimental results are in good agreement with estimation obtained from the modeling efforts. As expected, the results show that addition of NCCF or FM particles as fillers separately to the PDMS host matrix increases the elastic modulus of the composite. When both particle and fiber fillers are blended into the PDMS host matrix, the elastic moduli are very sensitive to the volume fraction of these components. For instance, the composite with volume fractions of 45.6% PDMS, 45.6% FM, and 8.8% NCCF, has a Young’s modulus \(E\) of \(\approx100\) MPa at room temperature, whereas for the composite with volume fractions of 47.4% PDMS, 42.0% FM, and 10.6% NCCF it is \(\approx70\) MPa at room temperature (Figure 2a).

The stiffness change ratios \(E_{\text{rigid}}/E_{\text{soft}}\) of the smart composites, in comparison with a two-component composite with 50% PDMS–50% FM volume fraction fabricated with the same procedure, are highlighted in Figure 2b. We found that in general the values of \(E_{\text{rigid}}/E_{\text{soft}}\) obtained in the experiments are very close to the predictions by the modeling efforts. In particular, for the two three-component composites, \(E_{\text{rigid}}/E_{\text{soft}}\) is \(20\times\) versus \(10\times\) according to experiments, and \(23\times\) versus \(16\times\) according to modeling. This good agreement indicates that in the process of making the FM particles, the oxide layer on the surface of the FM particles might not form. The oxide layer has higher melting temperature, which can lead to partial activation of FM particles at \(62\,^\circ\text{C}\) and result in a lower stiffness change ratio than predicted by the model.[18,54] As the FM particles are shear-mixed directly in part A of PDMS in this study (Experimental Section), the particles are less exposed to air during the fabrication process, which reduces the possibility of creating an oxide layer on their surfaces. Note that here there is only \(\approx2\%\) volume fraction difference in all three components, yet the difference in mechanical stiffness change ratios is much larger. One of the reasons for this is that, increasing the volume fraction of FM in the composite makes the material more rigid in the cold state and softer in the activated state, whereas addition of NCCF makes the composite more rigid in both states as there will be no phase change associated with NCCF before and after activation.

We also systematically characterized the electrical resistivity of the smart composites using experiments and theory. We use effective-medium theory to compute the electrical conductivity \(\sigma\) of the smart composites, which is trivially related to the electrical resistivity, i.e., \(\rho = 1/\sigma\), of the composites, by explicitly considering the microstructure of the smart composites including both volume fractions and their high-order spatial correlations. In particular, we use the strong-contrast formalism developed by Pham and Torquato,[55] which allows one to express the effective conductivity in terms of an infinite series involving individual phase properties and the \(n\)-point correlation functions.
These correlation functions provide the probability of finding a specific \( n \)-point configuration in the phase of interest in the material. Truncating the series at lower-order \( n \) allows one to derive approximations of the effective resistivity. Here \( S_n \) and other microstructural parameters involving integrals of \( S_n \) are computed directly from a 3D model of the smart composite, which is achieved by generating realistic 3D microstructure models of the composites using the hard-particle packing method, taking input from Figure 1b for geometrical information about the size distribution of the FM particles. See the Supporting Information for more details about this procedure.

Figure 3 shows the electrical resistivity \( \rho \) of the PDMS–NCCF and PDMS–FM–NCCF composites at different temperatures, both measured by experiments and predicted by theory. Note that due to the lack of temperature dependence data for electrical conductivity of NCCF, we only predicted the temperature dependence of the three-component composites (Table S1, Supporting Information). First, we notice that the PDMS–NCCF composites exhibit relatively low \( \rho \) with a strong dependence on temperature, unlike the PDMS–LMPA particle composite,[18] which evidences the effect of the shape of the inclusions on \( \rho \). We also see that \( \rho \) can be reduced to a much lower value than that of CPBE for the composite with volume fractions of 45.6% PDMS, 45.6% FM, and 8.8% NCCF. This material thus can be Joule-heated using a reasonable power requirement (Figure 1, Video S1, S2, S3, and S4), by adding NCCF to the mixture, the electrical conductivity of the composite is significantly enhanced although the total volume fraction of inclusions (FM particles and NCCF) is kept low (\( \approx 50\% \)). This allows one to tailor the electrical conductivity while maintaining high volume fraction of the elastomer matrix, which makes the composite less brittle and more robust for repeated use.

Finally, we demonstrate the high tunability in mechanical stiffness and the shape memory effect of the three-component smart composite using a simple beam bending test. Shape fixity, \( R_f \), and shape recovery, \( R_r \), are two main measures of the shape memory effect. Shape fixity is the extent to which a temporary shape is preserved and is calculated by \( R_f = \frac{\varepsilon_{fixity}}{\varepsilon_{load}} \times 100\% \), in which \( \varepsilon \) is the temporary strain after removal of the load and \( \varepsilon_{load} \) is the initial imposed strain at the soft state. Shape recovery is the ability of a material to return to its original shape after being in its temporary shape for some time and is quantified by \( R_r = \frac{\varepsilon_{recovery}}{\varepsilon_{load}} \times 100\% \), where \( \varepsilon_{recovery} \) is the permanent strain in the material after the shape recovery. Three rectangular specimens for each of the three compositions shown in Figure 2b were mounted in the material testing system and 10% uniaxial strain was applied to them in their soft state. The specimens were left to cool down for 15 min under tension and then were unmouted from the testing system. The retained strain in their temporary state were measured between two marked points on the specimens and \( R_r \) was calculated to be 86.58%, 72.62%, and 66.65% for composites with compositions 50% PDMS–50% FM, 45.6% PDMS–45.6% FM–8.8% NCCF, and 47.4% PDMS–42% FM–10.6% NCCF, respectively. The specimens were then softened using a heat gun to recover their original configuration.

![Figure 3. Electrical resistivity (\( \rho \)) of different compositions of PDMS–NCCF and PDMS–FM–NCCF composites at different temperatures. Both experimental data and theoretical predictions are presented. Error bars for experiments are based on at least five tests on each sample. Note that the data for PDMS–FM composites is not shown on this plot as they are not electrically conductive in the temperature range shown here.](https://www.advancedsciencenews.com/doi/fig)
and their new lengths were measured and $R$ was calculated to be 87.10%, 93.30%, and 96.65% for composites with compositions 50% PDMS–50% FM, 45.6% PDMS–45.6% FM–8.8% NCCF, and 47.4% PDMS–42% FM–10.6% NCCF, respectively. These values are in reasonable agreement with existing literature.[99] The trend observed in the shape fixity and shape recovery values compared with the volume fraction of the constituents shows that increasing the content of the NCCFs reduces the shape fixity and increases the shape recovery. Increasing the content of NCCFs in the composite increases the effective elastic modulus of the matrix as NCCF fillers remain solid even in the soft state of the composite, which brings down the fixity. Yet for the same reason, the NCCF fillers contribute to shape recovery, thus helping the composite structure return into its initial shape after the force is removed.

In Figure 4, we showcase that a thin strip of the three-component smart composite can hold a 50 g weight in the single cantilever beam configuration with a small displacement at the tip (panel 1, 2). When the strip is partially heated using a heat gun (panel 3), FM inclusions melt and the composite softens, which results in a large displacement at the tip of the beam under the same weight. The beam can hold the deformed configuration in the cold state (panel 4) even after the weight is removed. FM inclusions are solidified in the deformed state and the beam can maintain the new configuration with strain energy stored within. When heated above 62°C again, the beam recovers its initial undeformed configuration mostly and the stored strain energy in the smart composite is released. Here, this smart composite essentially performs as an entropic spring and creates the shape memory effect.[18]

Although the EMA and theory used here can roughly estimate the mechanical and electrical properties of the three-component smart composites that are experimentally characterized, we recognize that it is difficult to rely on these for systematic optimal design of the smart composite, when not only the volume fractions of the three components are varied but also the size distribution, aspect ratio, and even the fiber types are changed to achieve a whole set of desirable mechanical and electrical properties to satisfy specific needs according to different applications. Efforts on this aspect are clearly needed but beyond the scope of this work.

The three-component elastomer–particle–fiber smart composite we introduced here can have a combination of desirable properties including dynamically tunable mechanical stiffness, highly tunable electrical/thermal conductivity by varying volume fraction and temperature, improved mechanical and thermal robustness for repeated use, and shape memory effect. The composites can be selectively heated up/softened by applying electrical voltage through certain portion of the composite. We have demonstrated smart composites with $\approx 20 \times$ stiffness change, high electrical conductivity to allow for fast and portable activation through Joule heating, mechanical/thermal robustness for repeated use, and shape memory effect. This is by no means the optimal design and implementation of such a composite system, and future research would be expected to fully explore the potential of such a composite system.

**Experimental Section**

Fabrication: An ingot of FM (Roto144F, RotoMetals, Inc.) was heated up with part A of PDMS (Sylgard 184, Dow Corning) in a ceramic mortar on a hot plate to 70°C. A pestle was used to shears-mix the molten FM to 50–100 μm particles in part A of PDMS.[31] Then the mixture was transferred into a fridge at 5°C for 15 min till the FM particles solidify. Next, the mixture was taken out of the fridge and kept at the room temperature for 1 h. After that, part B of PDMS with a 1:1 ratio to part A and NCCF (Nickel wt% = 40%, length = 100 μm, diameter = 5 μm, Conductive Composites, Inc.) were added and blended with the mixture with a pestle thoroughly. In the next step, the uncured composite paste was flattened to a sheet and cured at 55°C for 5 h between two metal plates of a heat press machine (Carver 4389). Toward the end, with the sheet still under compression, the temperature was increased to 90°C for 40 min to enhance the electrical connection between the NCCF and the molten FM particles.

Testing: For stiffness characterization, rectangular samples with 3 mm thickness were cut from the composite sheets for tensile testing using an Instron 5969 testing system, which had a 50 kN load cell equipped with an extensometer with a gauge length of 25.4 mm. The samples were loaded in tension with a constant displacement rate of 2 mm min$^{-1}$, up to a strain of 2.5%, and then unloaded to the stress-free state. Bluehill 2 testing software was used to calculate the elastic moduli of samples from the stress–strain measurements automatically. To measure the electrical resistivity at different temperatures up to 115°C, the samples were cut with dimensions of 20 mm $\times$ 5 mm $\times$ 2.4 mm and placed into an oven. A two-point probe technique was adopted to measure the electrical resistivity.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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