

3D printed elastomer ternary composites

Naga Korivi,^{1,✉} Rifat Mahbub,² Zahra Ahmadi,² Soodabeh Azadehranjbar,² Jeffrey E. Shield,² Yuanyuan Ni,³ Yifan Yuan,³ Xiaoshan Xu,³ Limin Gong,⁴ Shaik Jeelani,⁵ and Vijay Rangari⁵

¹Department of Electrical and Computer Engineering, Tuskegee University, Tuskegee, Alabama, USA

²Department of Mechanical and Materials Engineering, University of Nebraska – Lincoln, Nebraska, Lincoln, USA

³Department of Physics and Astronomy, University of Nebraska – Lincoln, Lincoln, Nebraska, USA

⁴Department of Agriculture and Environmental Sciences, Tuskegee University, Tuskegee, Alabama, USA

⁵Department of Materials Science and Engineering, Tuskegee University, Tuskegee, Alabama, USA

✉ Email: nkorivi@tuskegee.edu

This paper describes the 3D printing of a ternary composite of polydimethylsiloxane (PDMS) and nanoparticles of iron oxide and barium titanate. The composite was printed using a commercially available 3D printer. Thermal curing of the composite during printing allowed for overall low process times of a few minutes. Scanning electron microscopy indicated uniform composite layers. The resulting composite films showed ferromagnetic behaviour, and applicability in magnetic actuation and piezoelectric energy harvesting.

Introduction: The emergence of flexible electronics in recent years has generated interest in composites of polymers and inorganic nano-scale materials or fillers. In this context, there has been great interest in composites of nano-materials and polydimethylsiloxane (PDMS), a flexible, transparent, chemically stable silicone elastomer useful for flexible electronics [1]. More recently, ternary composites of PDMS and two distinct nano-fillers are being investigated to create new materials/applications that exploit the characteristics of the individual components. Most of the prior related work has focused on ternary composites of PDMS, carbon, graphene-based materials for applications in sensing of strain, pressure and temperature, among others [1–3]. There have been a few efforts on other ternary material systems, such as those involving PDMS/barium titanate/carbon nanotubes, and PDMS/calcium copper titanate/carbon nanotubes as high dielectric constant and low dielectric loss materials [4, 5]. Considering their applicability, there is clearly a need and scope for further development of new PDMS-based ternary composites. Another important aspect to consider is the fabrication of these ternary composites. Till date, these composites have been made by conventional methods such as screen-printing, solution casting and moulding, among others [2–4, 6, 7]. The recent emergence of 3D printing has provided an economical and sustainable way to make polymer composites. Compared to most conventional fabrication methods, 3D printing techniques allow for increased levels of rapid prototyping, patterning and dimensional control. However, to the best of our knowledge, there have been no reports on 3D-printed ternary PDMS composites till date.

To summarize the present state of art, there is a need to develop new PDMS-based ternary composites using methods like 3D printing. This paper reports the development of a novel 3D-printed composite of PDMS and nanoparticles of barium titanate (BTO or BaTiO₃) and iron oxide (IO or Fe₂O₃). The inclusion of a piezoelectric nano-filler (BaTiO₃) and a magnetic nano-filler (Fe₂O₃) is designed to impart multifunctionality to the resulting composite. The 3D printing of the composite is done using a commercially available 3D printer. The resulting composite has been characterized for its properties and some potential applications are demonstrated in magnetic actuation and piezoelectric energy generation.

Experimental: Nanoparticles of BaTiO₃ and Fe₂O₃ were obtained from Nanostructured & Amorphous Material Inc., USA. PDMS (Sylgard 184, Corning) was acquired from Ellsworth Adhesives, USA. The BaTiO₃ and Fe₂O₃ nanoparticles were taken in 1:1 ratio by weight

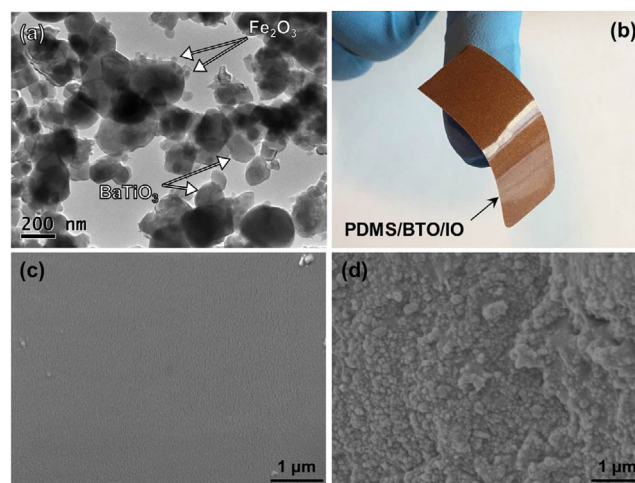


Fig. 1 (a) Bright-field TEM image of BaTiO₃ and Fe₂O₃ nanoparticle mixture. (b) Photograph of 3D-printed PDMS/BTO/IO composite. SEM images of 3D-printed composite showing (c) surface; (d) cross-section. BaTiO₃, barium titanate; Fe₂O₃, iron oxide; PDMS, polydimethylsiloxane; TEM, transmission electron microscope.

and the combined mixture was sintered at 600°C for 3 h, followed by ball milling. The morphology of the nanoparticle mixture was studied using transmission electron microscope (TEM JEOL 2010). The nanoparticle mixture was combined with PDMS pre-polymer in 50:50 ratio by weight. The blend was sonicated and the curing agent for PDMS was added to it. The composite mixture was fed into a disposable printing syringe which had a Luer-Lok tip with 1.5-mm diameter nozzle. The syringe was incorporated into an extrusion printing head of a 3D printer (Hydra 16A, Hyrel USA). The 3D models of test samples were designed using computer-aided design (CAD) software and supplied to the 3D printer. The printing was done using rectilinear fill patterns with 100% fill density, print speed of 10 mm/s, flow rate of 0.5 mL/min. The base plate temperature was maintained at 85°C during the printing. The printed composite is referred to as PDMS/BTO/IO. Surface and cross-sections of the 3D-printed PDMS/BTO/IO composite were studied using a scanning electron microscope (SEM, JEOL JSM 7200F). The 3D-printed PDMS/BTO/IO composite was also studied by x-ray diffraction (XRD, Rigaku D/MAX 2200 diffractometer), superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL), polarization-electric field hysteresis measurements (Precision RT66C Ferroelectric Tester).

Results and discussion: The TEM images (Figure 1a) of the Fe₂O₃ and BaTiO₃ nanoparticle mixture indicated that the Fe₂O₃ nanoparticles were in the 30 to 50 nm size range, while the BaTiO₃ nanoparticles were larger, around 100 to 200 nm. The particles were mostly spherical in shape. The printed PDMS/BTO/IO composite films visually appeared smooth and uniform, without obvious defects such as bubbles or voids (Figure 1b). SEM imaging performed on the surface of printed composites confirmed their uniformity (Figure 1c). SEM imaging of the cross-section of composite films indicated the mostly uniform dispersion of the nanoparticles in the polymer matrix (Figure 1d). However, there were a few areas of nanoparticle agglomeration observable in the PDMS matrix.

The structure of the PDMS/BTO/IO composite was studied using the XRD technique. The XRD spectrum of the PDMS/BTO/IO composite (Figure 2a) showed the characteristic spectral peaks of PDMS, BaTiO₃ (circle markers) and Fe₂O₃ (triangle markers). A broad peak at a 2θ value of 12.1° is from the PDMS due to its partly crystalline nature. The reflections at 2θ values of 44° and 46° correspond to the (002) and (200) planes of BaTiO₃, indicative of its tetragonal nature [8]. The peaks of Fe₂O₃ are typical of α-Fe₂O₃ [9]. SQUID magnetometer measurements on the PDMS/BTO/IO composite yielded hysteresis loop of magnetic moment versus magnetic field at 300 K, as shown in Figure 2b. The printed composite showed ferromagnetic behaviour (Figure 2b) with a coercivity of 191 Oe and remanence of 2.4 emu/g. The ferromagnetic

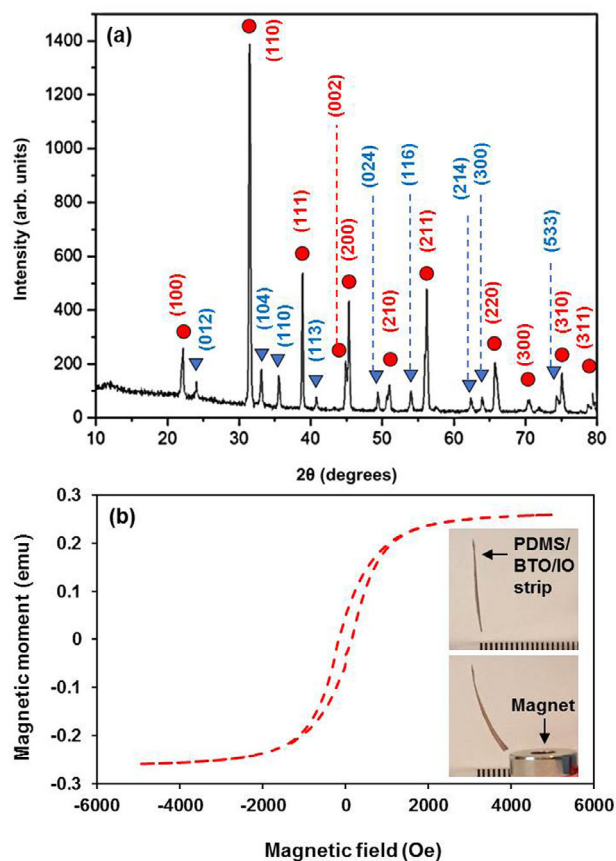


Fig. 2 (a) XRD spectrum of 3D-printed PDMS/BTO/IO composite showing the representative peaks of barium titanate (circle markers) and iron oxide (triangle markers). (b) Magnetic moment as a function of magnetic field for the PDMS/BTO/IO composite. (inset) Actuation of a composite strip under magnetic field. The scale is in mm. PDMS, polydimethylsiloxane.

property is attributed to the Fe_2O_3 nanoparticles. The PDMS/BTO/IO composite was evaluated for magnetic actuation. A strip of composite ($15 \text{ mm} \times 2 \text{ mm} \times 0.05 \text{ mm}$) was suspended from a non-magnetic support such that the other end of the strip was free. When a cylindrical magnet (1.2 T, NdFeB) was brought towards the free end of the composite strip, the free end underwent a deflection of a few mm, as shown in Figure 2b (inset). These preliminary observations suggest the composite can have applications in magnetic actuation.

Polarization (P) versus electric field (E) hysteresis loops obtained at 1 Hz from PDMS/BTO/IO composite and neat PDMS are shown in Figure 3a. The extracted maximal polarization values are 0.008, and $0.011 \mu\text{C}/\text{cm}^2$ for neat PDMS, and the PDMS/BTO/IO composite respectively. The P-E loops obtained from the PDMS/BTO/IO composite show linear capacitor characteristics, similar to P-E loops reported elsewhere from PDMS/BaTiO₃ composites [10].

The limited polarization exhibited by the composite is attributed to the large fraction of inactive polymer in it [10]. The dielectric constant of the composite was 5.8, compared to 4.2 for neat PDMS. This is in line with prior reports on PDMS/BaTiO₃ composites which showed dielectric constant of 4.27 with a 23 wt% BaTiO₃ loading [11]. The limited dielectric constant of the composite is attributed to the electrically insulating nature of the PDMS [12].

A piezoelectric energy generator (PENG) device was made by placing electrodes on both sides of a composite layer ($10 \text{ mm} \times 7 \text{ mm} \times 0.050 \text{ mm}$ thick), as shown in Figure 3b (inset). A repeated finger tapping force (0.1–0.2 N) was manually applied on the device surface. The resulting characteristic voltage spikes are shown in Figure 3b. The maximum output voltage is 0.31 V (positive) and 0.09 V (negative), with a maximum peak-to-peak voltage of 0.4 V. This output voltage though modest is similar to that of other 3D-printed PDMS/BaTiO₃ composite piezoelectric generator devices (0.385 V peak-to-peak under $>890 \text{ N}$ force on a 3-mm-thick PDMS/BaTiO₃ composite layer with 50 wt% BaTiO₃ nanoparticles) reported recently [13].

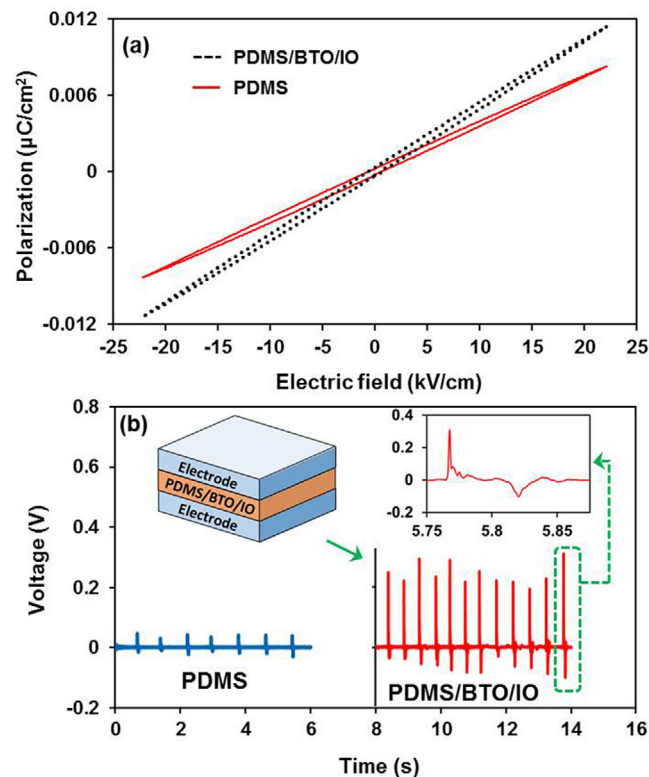


Fig. 3 (a) P-E hysteresis loops of PDMS and PDMS/BTO/IO. (b) Output performance of PDMS/BTO/IO piezoelectric energy generator. PDMS, polydimethylsiloxane.

The preliminary observations described here indicate that the 3D-printed PDMS/BTO/IO composite can be applied for piezoelectric energy generation. It should be noted that there may be a certain loading level of BTO nanoparticles and optimal thickness of the composite which will yield the best performance in piezoelectric energy generation. Our ongoing and future studies are expected to determine these optimal conditions, and help improve the overall properties of the material. Further improvements in the material's properties are possible. Overall, the PDMS/BTO/IO composite described here shows potential as a multifunctional material.

The 3D printing process used to make the PDMS/BTO/IO composite offers good dimensional control, with printed patterns closely following the set dimensions of the original pattern on the CAD software file. The printing process itself typically takes a few minutes, from loading the syringe into the printer, followed by the actual printing. The curing is in-situ since the printer's base plate temperature is maintained at a higher temperature than the conventional curing temperature for PDMS. There is no need to transport the printed patterns to any external curing equipment. Prior reports employed post-printing curing of 3D-printed PDMS/iron composites at room temperature for 48 h or at elevated temperatures in external thermal ovens [14, 15]. Extensive curing times after printing add on to the overall fabrication duration, and may not be suitable for rapid prototyping applications. More recently, researchers have reported 3D-printed PDMS/BTO composites that were subjected to post-printing curing at 70°C for 90 min in external curing chamber under ultraviolet light [13]. Generally, there is a need to minimize any post-printing processing or to avoid it altogether. This is because post-processing has been identified as a major barrier in the industrial advancement of 3D printing [16]. The present work does not employ any post-processing and therefore improves on the existing state of art.

Due to its ability to address customizability and application-specific needs, 3D printing has emerged as a promising method to manufacture flexible electronic devices [17]. This work demonstrates for the first time the feasibility of making PDMS-based ternary composites using 3D printing, and therefore constitutes an advance in technology. Other kinds of new ternary composites can also be printed in a similarly facile manner, potentially enabling new application avenues including novel flexible electronic devices.

Conclusions: We have reported on a novel ternary composite of PDMS, Fe₂O₃ and BaTiO₃ nanoparticles fabricated by 3D printing. The composite exhibited ferromagnetic behaviour. Composite strips showed physical actuation under an applied magnetic field. The composite produced a modest voltage output under small finger tapping force, showing applicability in piezoelectric energy generation. This work opens up possibilities of making new multifunctional, multi-component silicone elastomer composites by 3D printing.

Author contributions: Naga Srinivas Korivi: Conceptualization, Funding acquisition, Investigation, Methodology, Supervision, Writing original draft. Rifat Mahbub: Investigation. Zahra Ahmadi: Investigation. Soodabeh Azadehhanjbar: Investigation. Jeffrey Shield: Funding acquisition, Methodology, Resources, Supervision, Writing review - editing. Yuanyuan Ni: Investigation. Yifan Yuan: Investigation. Xiaoshan Xu: Methodology, Resources, Supervision, Writing review - editing. Limin Gong: Investigation. Shaik Jeelani: Funding acquisition. Vijay Rangari: Funding acquisition, Resources, Writing review - editing.

Acknowledgements: The authors acknowledge valuable contributions from Mr. Emery Utterback, Tuskegee University. This work was supported by the National Science Foundation, Division of Materials Research, (grant NSF-PREM #1827690).

Conflict of interest: The authors declare no conflict of interest.

Data availability statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

© 2023 The Authors. *Electronics Letters* published by John Wiley & Sons Ltd on behalf of The Institution of Engineering and Technology.

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made. Received: 14 January 2023 Accepted: 15 February 2023
doi: 10.1049/ell2.12749

References

- Kumpika, T., et al.: Stretchable and compressible strain sensors for gait monitoring constructed using carbon nanotube/graphene composite. *Mater. Res. Express*. **7**, 035006 (2020)
- Liu, X., Li, C., Wang, Z., Li, Y., Huang, J., Yu, H.: Wide-range flexible capacitive pressure sensors based on origami structure. *IEEE Sens. J.* **21**, 9728–9807 (2021)
- Wu, L., et al.: Screen-printed flexible temperature sensor based on FG/CNT/PDMS composite with constant TCR. *J. Mater. Sci. Mater.* **30**, 9593–9601 (2019)
- Tang, Y., et al.: Enhanced dielectric performance of polydimethylsiloxane-based ternary composites films via tailored hydrogen bonds between carbon nanotube and barium titanate as modified fillers. *J. Vinyl Addit. Technol.* **28**, 184–195 (2022)
- Liu, G., et al.: Enhanced dielectric performance of PDMS-based three-phase percolative nanocomposite films incorporating a high dielectric constant ceramic and conductive multi-walled carbon nanotubes. *J. Mater. Chem. C* **6**, 10829–10837 (2018)
- Kantarak, E., et al.: Fabrication, design and application of stretchable strain sensors for tremor detection in parkinson patient. *Appl. Compos. Mater.* **27**, 955–968 (2020)
- Barshutina, M., et al.: Biocompatible, electroconductive, and highly stretchable hybrid silicone composites based on few-layer graphene and CNTs. *Nanomaterials* **11**, 1143 (2021)
- Hongo, K., Kurata, S., Jomphoak, A., Inada, M., Hayashi, K., Maezono, R.: Stabilization mechanism of the tetragonal structure in a hydrothermally synthesized BaTiO₃ nanocrystal. *Inorg. Chem.* **57**, 5413–5419 (2018)
- Hjiri, M. Highly sensitive NO₂ gas sensor based on hematite nanoparticles synthesized by sol–gel technique. *J Mater Sci. Mater Electron.* **31**, 5025–5031 (2020)
- Khatua, D.K., Kim, S-J.: A high performance piezoelectric–triboelectric hybrid energy harvester by synergistic design. *Energy Adv.* **1**, 613–622 (2022)
- Tantraviwat, D., et al.: Tuning the dielectric constant and surface engineering of a BaTiO₃/Porous PDMS composite film for enhanced triboelectric. *ACS Omega* **6**, 29765–29773 (2021)
- Zhang, X., Le, M., Zahhaf, O., Capsal, J., Cottinet, P., Petit, L.: Enhancing dielectric and piezoelectric properties of micro-ZnO/PDMS composite-based dielectrophoresis. *Mater. Des.* **192**, 108783 (2020)
- Renteria, A., et al.: Direct ink write multi-material printing of PDMS-BTO composites with MWCNT electrodes for flexible force sensors. *Flex. Print. Electron.* **7**, 015001 (2022)
- Liu, F., Alici, G., Zhang, B., Beirne, S., Li, W.: Fabrication and characterization of a magnetic micro-actuator based on deformable Fe-doped PDMS artificial cilium using 3D printing. *Smart Mater. Struct.* **24**, 035015 (2015)
- Roh, S., Okello, L., Golbasi, N., Hankwitz, J., Liu, J., Tracy, J., Velez, O.: 3D-printed silicone soft architectures with programmed magneto-capillary reconfiguration. *Adv. Mater. Technol.* **4**, 1800528 (2019)
- Stavropoulos, P., et al.: Addressing the challenges for the industrial application of additive manufacturing: Towards a hybrid solution. *Int. J. Lightweight Mater. Manuf.* **1**, 157–168 (2018)
- Espera, A., Dizon, J.R., Valino, A., Advincula, R.: Advancing flexible electronics and additive manufacturing. *Jpn. J. Appl. Phys.* **61**, SE0803 (2022)