Single-Mode, 700%-Stretchable, Elastic Optical Fibers Made of Thermoplastic Elastomers

Soroush Shabahang,* Fatima Clouser, Farzaneh Shabahang, and Seok-Hyun Yun

Optical fibers made of thermoset elastomeric materials can offer extremely high stretchability not possible with conventional glass and plastic optical fibers. However, such elastomer fibers have so far been made with large mm-scale diameters, which limit their potential utilities. Here, fabrication of small-diameter (< 200 μ m), core-clad optical fibers using a thermal drawing of transparent thermoplastic elastomers is demonstrated. The single-mode optical fibers fabricated by this method are highly elastic and durable against strain up to 700%. Furthermore, a composite thermoplastic-thermoset elastic optical fiber is also presented, in which the advantageous properties of both families of elastomers are combined. These optical fibers may be useful for short-distance, mechanically flexible, optical interconnections in biomedical, wearable, or implantable photonic devices.

1. Introduction

There have been great interests in flexible optical fibers and waveguides for numerous biomedical applications, such as health-monitoring wearables,^[1-4] soft implants,^[5–8] soft robotics and prosthetics,^[9,10] body motion sensors,^[11–13] and artificial skin.^[14] For these applications, ultralow optical loss demanded in telecommunications is not necessary, and it is highly desirable to match the mechanical properties of the optical fibers to soft tissues with which the photonic devices are in contact. For these applications, optically transparent elastomers have been considered promising materials. The most well-known materials are thermoset elastomers, such as polydimethylsiloxane (PDMS) and transparent hydrogels, with tissue-matching, low mechanical moduli (10 kPa–1 MPa), and relatively low optical losses (0.2–2 dB cm⁻¹).^[15] Thermoset elastomers

Charlotte, NC 28223, USA

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adom.202100270.

© 2021 The Authors. Advanced Optical Materials published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adom.202100270

tomeric optical waveguides can be fabricated using various methods including molding,^[7,11,16] semi-cured drawing,^[17,18] laser writing,^[19] lithography,^[20,21] or 3D printing.^[22] Moreover, the ease of fabrication allows for more complex devices, such as stretchable optical waveguides integrated with vertical-cavity surfaceemitting lasers, photodiodes^[23] and microfluidic channels.^[24] It is also easy to incorporate micro- or nanoparticles and functional materials into the polymer network.^[25] However, it has been challenging to fabricate small-diameter optical fibers using these methods. This is primarily because of the low mechanical strength of thermoset materials and

the difficulty of handling highly flexible elastomer materials with small dimensions.

On the other hand, optically transparent thermoplastic elastomers (TPEs), which differ from thermoset elastomers, are promising materials for fabricating elastic optical fibers.^[26,27] Thermal drawing of thermoplastic materials allows fabrication of fine fiber features that are not attainable with the molding of thermoset polymers.^[28] Some other advantages of using TPEs over thermoset elastomers include the possibility of thermal postprocessing of fibers for fiber-device fabrication, scalability of the fiber structure, and long-length uniform fiber fabrication.^[29-32] Small-diameter fibers (< 200 µm) offer several advantages. First of all, thinner fibers are generally better suited for such applications as body strain sensing, as the required force to stretch an elastic optical fiber decreases with the square of the fiber thickness. For strain sensing applications, based on scattering,^[10,33] absorption,^[11,12,25] and bending^[33] optical losses, thinner fibers could lead to higher sensitivity. Furthermore, the number of optical modes an optical fiber guides is proportional to the square of the diameter of the core. Many photonics devices require single-mode operation.^[34] For single-mode guiding, the diameter of the core is typically less than several microns. Elastic single more fibers can serve in an all-fiber tunable optical delay line or tunable dispersion device.

Here, we present the fabrication of small-diameter, flexible, and highly stretchable optical fibers using the thermal drawing of TPE. In particular, we demonstrate single-mode light guiding, to our knowledge for the first time, in elastomer fibers. The single-mode fibers consist of the core and cladding prepared from two different types of TPEs with similar melting temperatures. The TPE fibers withstand elongations of several times the original length and are stable at room temperature.

Dr. S. Shabahang, F. Clouser, Prof. S.-H. Yun Wellman Center for Photomedicine Massachusetts General Hospital Department of Dermatology Harvard Medical School 65 Landsdowne Street, Cambridge, MA 02139, USA E-mail: sshabahang@mgh.harvard.edu F. Shabahang Department of Mechanical Engineering and Engineering Science University of North Carolina at Charlotte



2. Results

We tested several transparent TPE to find a pair of low-loss polymers with approximately similar refractive index (*n*) values for weakly guiding in a standard core-clad structure. The index *n* was determined as the ratio of the real to apparent (optical) thickness of polymer slabs using an optical microscope. Each sample with about 3 mm in thickness was gently placed between two glass slides that had ink marks on their inner sides. As a sample stage was moved vertically, the apparent thickness was measured as the distance between the sharp images of the ink marks with the sample in place, and the real sample thickness was measured by displacing the sample and measuring the distance between the glass slides with the air in between. Among the elastomers tested, we selected "Star-Clear 1044-0000" ($n = 1.52 \pm 0.01$) and "StarClear 1030-0000" $(n = 1.50 \pm 0.01)$ as the core and cladding materials, respectively. Both materials are RoHS-compliant UV-resistant rubbery soft polymers and are thermally consistent with each other for co-drawing (melting points according to the manufacturer datasheet: 185-205 °C). The spectral transmission of the elastomers, measured using a spectrophotometer (Figure 1a), shows an attenuation of 1–1.5 dB cm⁻¹ in the visible wavelength range and $< 1 \text{ dB cm}^{-1}$ in the near IR wavelengths, excluding reflection loss at the material-air interfaces. Like other elastic materials,^[35] the optical refractive indices of the elastomers changed slightly under large strain. For both materials, the refractive index in the direction perpendicular to the elongation was measured to decrease by \approx 2 and 4% at the axial strain of 50 and 100%, respectively (Figure 1b).

Our fiber fabrication steps consist of polymer molding, preform fabrication, and thermal drawing of the fiber preform, as illustrated in Figure 1c. In the molding process, polymer pellets were cut into < 1-mm-thick pieces, washed with ethanol, and dried inside a vacuum oven at 60 °C for 1 h. The dried polymer pieces were inserted in a glass mold and heated in the vacuum oven for 12 h at 200 °C, while a 400 g metallic weight was placed on top to squeeze the molten material inside the mold. The reshaped material was cooled down to room temperature and then removed from the mold. For the core, glass molds with an inner diameter of 0.75 mm was used. For cladding, the glass mold had an inner diameter of 3.2 mm, and a solid rod with a diameter of 0.8 mm was placed in the middle of the mold so that the final polymer product comes with a tubular shape with an inner and outer diameter of 0.8 and 3.2 mm, respectively. The fabricated core preform was inserted into the inner hole of the cladding preform. This forms a preform for core-clad fibers.

We used a small horizontal thermal drawing setup, similar to one in fiber tapering machines, which is appropriate for our small preforms with a few millimeters of thickness and makes it easy to control the drawing parameters. More importantly, TPEs have generally lower viscosity values than rigid thermoplastics and glasses above their softening points,^[29] and this property makes it difficult to support the weight of the bottom necking of the preform and the drawn fiber at the beginning of the draw. However, this approach may not be effective for thick preforms because the weight of the softened material can deform the preform. We used a soldering iron with a customized half-cylinder 1-cm-long tip as a heater, set at 250 °C (the actual temperature of the heat zone). The preform was fed manually into the heating zone at a low speed of $\approx 0.5 \text{ mm s}^{-1}$ while the distal end of the fiber was pulled at a speed of $5-10 \text{ cm s}^{-1}$. These drawing speeds produced core-clad fibers with an outer diameter of 220-270 µm and a core diameter of 50-60 µm, a similar dimension as conventional plastic or glass multimode fibers.



Figure 1. Fiber materials and fabrication. a) Spectral transmission of the core and cladding thermoplastic polymers. Inset is a test sample. b) Variation of the n of the core polymer versus strain (sample dimensions $3 \times 3 \times 10$ mm). n is measured perpendicular to the strain direction. c) Fabrication steps of thermoplastic elastic fiber, including: 1) Preparation of the preform core and cladding via polymer molding in vacuum, 2) inserting the preform core inside the cladding tube (core diameter = 0.75 mm, cladding inner diameter = 0.8 mm and cladding outer diameter = 3.2 mm), and 3) thermal drawing of the preform.

www.advancedsciencenews.com



Figure 2. Single-mode light guidance. a) two-step fabrication of small core fiber for which the core of the second preform is a large-core-fiber obtained by drawing the first preform. b) Cross-section of the large core fiber transmitting 635 nm laser light. c) Single-mode guidance of 635 nm laser light in a small core fiber. d) The output profile of a fiber with a slightly larger core size, showing the higher-order LP₁₁ mode. (Inset shows a schematic of the setup for (b–e)). e) Comparing the normalized spectra of 635 nm laser light before and after the fiber in (c) to verify single-mode guidance and no modal interference in the frequency domain. f) Spectral loss characterization of the molded polymers along with optical loss of the large and small core fibers at 635 nm.

Given the index difference of ≈ 0.02 between the core and the clad, for single-mode guiding our target core diameter was 5 µm. To achieve this small core size, we used an over-jacketing method. The multimode fiber drawn from the preform was inserted into a second jacketing tube prepared in the same method as we used to make the cladding preform. The inner diameter of the jacketing tube was matched to the outer diameter of the multimode fiber (Figure 2a). Drawing the jacketed preform with the same draw-down ratio yielded an optical fiber with a clad diameter of $\approx 200 \,\mu\text{m}$ and a core diameter of $\approx 5 \,\mu\text{m}$. Figure 2b,2c shows the pictures of end facets of the large- and small-core fibers, when a broadband laser light (12-nm bandwidth centered at 635 nm) was launched into the other facet of the fibers using an objective lens. The output intensity profile shows the fundamental fiber mode. When the input light coupling was changed by translating the objective lens, only the intensity was changed but the mode profile did not change. Figure 2d shows the output beam profile from a fiber with a core diameter of $\approx 6 \,\mu m$, which is comprised largely of the LP11 mode. Therefore, the 5 µm core diameter is considered as the approximate threshold for single-mode guidance. Finally, comparing the spectrum of the light before and after the single-mode fiber did not show any modal interference pattern (Figure 2e). These results provide evidence for single-mode guidance.

The optical propagation loss of the fibers was measured via cutback technique at 635 nm. The measured loss coefficients were 1.2 dB cm⁻¹ for the large-core multimode fibers and 1.9 dB cm⁻¹ for small-core single-mode fibers (Figure 2f). These values are higher than the intrinsic material loss that we measured with bulk polymer samples of different thicknesses (3 mm and 15 mm) prepared by polymer molding (Figure 2f). The higher loss of the single-mode fiber may be due to the increased contribution of scattering at the core/cladding interface with the decreased beam area. The total light loss originates from two major causes: material absorption and light scattering. In a core-only fiber, considering the total internal reflection from the polymer-air interface, about 56% of light propagating in all directions remains confined inside the polymer, and about 35% of the Rayleigh scattered light would be guided in the forward direction. To study the contribution of optical absorption from the total loss, we collected the forward scattered light using a detector at the end of cladding-free samples. The tests on two samples of different lengths (3 mm and 5 cm) show that about 30% of the core polymer loss at 635 nm is due to material absorption.

The flexibility and super-elasticity of the fibers are illustrated in Figure 3. Due to the material's softness, the fiber can be bent over very small radii. The maximum elongation at break is \approx 700% for the core and \approx 900% for the cladding polymers (values provided by the vendor). Figure 3b shows the tensile-strength test for a small core fiber with 200 µm diameter, in which the fiber sample is pulled by a stepper motor on a rail, and the force is measured using a load cell (RB-Phi-203-100g Micro Load Cell). The tensile-strength test confirms the values provided by the vendor. The Young's modulus at 300% strain of the polymer is approximately 1 MPa. Therefore, to produce 300% strain on a 200- μ m-thick fiber only < 0.1 N force is required. This stiffness of TPE fibers is very close to the stiffness of soft tissues such as the human skin (0.1-0.9 MPa).^[36,37] Therefore, the mechanical property would be well suited for use in wearable or implantable photonic devices. For comparison, Young's modulus of





Figure 3. Fiber mechanical properties. a) A piece of flexible soft fiber relaxed on the ground with sharp curves without holding. b) Tensile-strength test for a 200-µm-thick fiber with an initial length of 46 mm. The elongation at break is more than 700%. The inset is a schematic of the test set-up. c) A 200-µm-thick elastic fiber stretched more than 4 times the original length.

conventional silica fibers is 73 GPa, even higher than those of hard bones (\approx 20 GPa).

Because both the core and cladding indices are affected similarly by strain, the light-guiding condition is maintained. However, as the fiber is stretched, the total transmission decreases, as expected from the Beer's law that the total transmission decreases exponentially with the propagation length at a constant loss coefficient. Interestingly, we found that the loss coefficient of our fibers is not constant but increased with strain because Rayleigh scattering increased with strain in our fiber materials. We did not observe any degradation or defects in the core/cladding interface after inspecting the fibers under a microscope and feel confident that the scattering is due to reversible changes in the fiber materials. Figure 4a shows the scattered light of 635 nm laser light in a bulk sample of the core polymer. As the sample was stretched, the brightness of scattered light increased. The images showed that the scatterers are uniformly distributed inside the bulk material. When a collimated white light, instead of the 635 nm laser, was launched into the sample, the color of scattered light seen from the side changed from blue to red along the fiber length, because the shorter wavelengths scatter more strongly, and the longer wavelength light propagates farther than shorter wavelength light. To explain this phenomenon, we hypothesize that with strain, the nano-pores in the polymer network are elongated and enlarged to induce stronger Rayleigh scattering. This hypothesis is supported by the fact that the refractive index of the polymer decreases by stretching, as shown in Figure 1b. This phenomenon was reversible. The sample went back to the low scattering state after releasing the strain.

When scattering is the dominant loss mechanism, and β is a scattering coefficient, then $dI(z)/dz = -\beta I(z)$, where

I(z) is light intensity along the propagation coordinate of z. The transmission in the log scale may be described as $T_{\rm dB}(l) = \log (I(l)/I(0)) = -\beta \cdot l$, where l is the length of the sample. Figure 4b shows the measured transmission of a bulk polymer sample used for the core as a function of strain: $\varepsilon = l/l_0 - 1$, where l_0 is the original length at the relaxed state. From the linear trend, we found that β increases quasi linearly with the magnitude of strain. We applied the linear $\beta(\varepsilon)$ function to single-mode optical fibers. Figure 4c shows the experimentally measured transmission of a single-mode fiber, which is largely explained by the light scattering coefficient increasing with the applied strain.

While thermoplastic polymers are well suited for thermal drawing into small diameters, as demonstrated above, thermoset polymers offer many favorable properties as mentioned in the Introduction. We explored the possibility of fabricating a composite fiber with a soft thermoplastic cladding and a thermoset core. For this purpose, a thermoplastic hollow preform was prepared by molding "StarClear 1030-0000" TPE, as described above. The preform had an inner and outer diameter of 2.8 and 8 mm, respectively. The preform hollow was obstructed by a screw to trap the air and eliminate hollow collapsing (Figure 5a). After thermal drawing, a hollow fiber with an inner diameter of $< 10 \ \mu m$ is obtained (Figure 5b). A section of the fiber with a small hollow diameter (<10 µm) was filled with "Gelest PP2-OE50" thermoset elastomer and cured at 55 °C for 4 h (Figure 5c). The refractive index of the core material is 1.5 in the visible wavelengths. The optical properties of the fiber are similar to that of the core elastomer. The optical loss was measured to be 1 dB cm⁻¹ at 635 nm. we did not observe any enhanced material scattering after stretching. The core thermoset material is less stretchable than the cladding ADVANCED SCIENCE NEWS _____





Figure 4. Light scattering in the core polymer versus strain. a) Top is the schematic of the experimental setup to visualize the light scattering in polymer samples; middle image shows scattering of red laser light in the core material. Stretching the sample increases the scattering and the sample looks brighter; bottom image shows white light scattering in a 1-mm-thick rod, forming a rainbow color pattern. b) Measured the optical transmission (green) and the corresponding optical scattering (blue) of a bulk polymer sample (core polymer) versus strain. c) The measured optical loss of an elastic single-mode fiber versus strain (red circles) and the calculated values (blue circles) from the fiber loss measured in the relaxed state and the strain-dependent scattering loss of the bulk polymer obtained in (b). The insets show the optical modes in the output facet.

TPE material. Within the acceptable strain range up to 75% elongation, we did not observe any significant increase of loss due to stretching. The fiber guided a single mode at 635 nm (Figure 5d).

3. Conclusion

We have demonstrated the first single-mode elastic optical fibers thermally drawn from thermoplastic elastomer preforms. Compared to conventional silica fibers, the elastomer fibers are elongated up to 700% with a small force of <0.2 N, with 5 orders of magnitude lower Young's modulus than conventional silica fibers. The propagation loss of these fibers is 1.2–1.9 dB cm⁻¹, primarily arising from the Rayleigh scattering of nano-pores in the loose polymer network of TPE. These fibers may prove useful for applications that require mechanical flexibility and short-distance light propagation, such as optical interconnections in flexible wearables, all-fiber tunable delay lines, and strain sensors.



Figure 5. Composite elastic fibers (thermoset elastomer core & thermoplastic elastomer cladding). a) Schematic shows the thermal drawing of an elastic hollow fiber. The screw is used for trapping the air and avoid collapsing the hollow. The inner and outer diameters of the molded preform are 2.8 & 8 mm, respectively. b) A section of the drawn fiber. c) Filling the hollow of the fiber with PP2-OE50 thermoset elastomer. d) Left to right: cross-section and zoomed-in images of the small core fiber and the single-mode guidance of 635 nm laser light in the fiber core.

ADVANCED SCIENCE NEWS _____

Acknowledgements

The work was supported by the Air Force Office of Scientific Research (AFOSR; FA9550-20-1-0063), National Institutes of Health (NIH; R01CA192878, P41 EB015903), and the Korea Institute of Science and Technology (KIST ORP Program, 2E27830, 2E27833).

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.

Keywords

fifiber optics, flexible optical fibers, light scattering, optical devices, strechable devices, thermoplastic elastomers

Received: February 5, 2021 Revised: March 10, 2021 Published online:

- [1] S. H. Yun, S. J. J. Kwok, Nat. Biomed. Eng. 2017, 1, 0008.
- [2] A. K. Yetisen, N. Jiang, A. Fallahi, Y. Montelongo, G. U. Ruiz-Esparza, A. Tamayol, Y. S. Zhang, I. Mahmood, S.-A. Yang, K. S. Kim, H. Butt, A. Khademhosseini, S.-H. Yun, *Adv. Mater.* **2017**, *29*, 1606380.
- [3] J. Guo, B. Zhou, C. Yang, Q. Dai, L. Kong, Adv. Funct. Mater. 2019, 29, 1902898.
- [4] M. Elsherifa, M. U. Hassan, A. K. Yetisen, H. Butt, Biosens. Bioelectron. 2019, 137, 25.
- [5] M. Choi, J. W. Choi, S. Kim, S. Nizamoglu, S. K. Hahn, S.-H. Yun, *Nat. Photonics* 2013, *7*, 987.
- [6] C. Lu, S. Park, T. J. Richner, A. Derry, I. Brown, C. Hou, S. Rao, J. Kang, C. T. Moritz, Y. Fink, P. Anikeeva, *Sci. Adv.* 2017, *3*, e1600955.
- [7] M. Choi, M. Humar, S. Kim, S.-H. Yun, Adv. Mater. 2015, 27, 4081.
- [8] L. Wang, C. Zhong, D. Ke, F. Ye, J. Tu, L. Wang, Y. Lu, Adv. Opt. Mater. 2018, 6, 1800427.
- [9] H. Zhao, K. O'Brien, S. Li, R. F. Shepherd, Sci. Robot. 2016, 1, eaai7529.
- [10] C. To, T. Hellebrekers, J. Jung, S. J. Yoon, Y.-L. Park, IEEE Robot. Autom. Lett. 2018, 3, 3821.
- [11] J. Guo, M. Niu, C. Yang, Optica 2017, 4, 1285.



- [12] D. Wang, B. Sheng, L. Peng, Y. Huang, Z. Ni, Polym. J. 2019, 11, 1433.
- [13] J. Guo, K. Zhao, B. Zhou, W. Ning, K. Jiang, C. Yang, L. Kong, Q. Dai, Adv. Opt. Mater. 2019, 7, 1900086.
- [14] J. Missinne, G. V. Steenberge, B. V. Hoe, K. V. Coillie, T. V. Gijseghem, P. Dubruel, J. Vanfleteren, P. V. Daele, *Proc. SPIE* 2009, 7221, 722105.
- [15] S. Shabahang, S. Kim, S.-H. Yun, Adv. Funct. Mater. 2018, 28, 1706635.
- [16] D. Pérez-Calixto, D. Zamarrón-Hernández, A. Cruz-Ramírez, M. Hautefeuille, J. Hernández-Cordero, V. Velázquez, M. Grether, *Opt. Mater. Express* **2017**, *7*, 1343.
- [17] J. Paek, J. Kim, Nat. Commun. 2014, 5, 3324.
- [18] I. Martincek, D. Pudis, M. Chalupova, IEEE Photonics Technol. Lett. 2014, 26, 1446.
- [19] G. Panusa, Y. Pu, J. Wang, C. Moser, D. Psaltis, *Opt. Mater. Express* 2019, 9, 128.
- [20] S. Valouch, H. Sieber, S. Kettlitz, C. Eschenbaum, U. Hollenbach, U. Lemmer, Opt. Express 2012, 20, 28855.
- [21] D. A. Chang-Yen, R. K. Eich, B. K. Gale, J. Lightwave Technol. 2005, 23, 2088.
- [22] K. Swargiary, P. Jarutatsanangkoon, P. Suwanich, R. Jolivot, W. S. Mohammed, Appl. Opt. 2020, 59, 122.
- [23] J. Missinne, S. Kalathimekkad, B. V. Hoe, E. Bosman, J. Vanfleteren, G. V. Steenberge, Opt. Express 2014, 22, 4168.
- [24] S. M. Azmayesh-Fard, E. Flaim, J. N. McMullin, J. Micromech. Microeng. 2010, 20, 087002.
- [25] J. Guo, X. Liu, N. Jiang, A. K. Yetisen, H. Yuk, C. Yang, A. Khademhosseini, X. Zhao, S.-H. Yun, *Adv. Mater.* **2016**, *28*, 10244.
- [26] A. Leber, B. Cholst, J. Sandt, N. Vogel, M. Kolle, Adv. Funct. Mater. 2019, 29, 1970030.
- [27] Y. Qu, T. Nguyen-Dang, A. G. Page, W. Yan, T. D. Gupta, G. M. Rotaru, R. M. Rossi, V. D. Favrod, N. Bartolomei, F. Sorin, *Adv. Mater.* **2018**, *30*, 1707251.
- [28] J. J. Kaufman, G. Tao, S. Shabahang, D. S. Deng, Y. Fink, A. F. Abouraddy, *Nano Lett.* 2011, *11*, 4768.
- [29] S. Shabahang, J. J. Kaufman, D. S. Deng, A. F. Abouraddy, Appl. Phys. Lett. 2011, 99, 161909.
- [30] J. J. Kaufman, G. Tao, S. Shabahang, E.-H. Banaei, D. S. Deng, X. Liang, S. G. Johnson, Y. Fink, A. F. Abouraddy, *Nature* 2012, 487, 463.
- [31] S. Shabahang, G. Tao, J. J. Kaufman, Y. Qiao, L. Wei, T. Bouchenot, A. P. Gordon, Y. Fink, Y. Bai, R. S. Hoy, A. F. Abouraddy, *Nature* 2016, 534, 529.
- [32] S. Shabahang, S. Forward, S.-H. Yun, Opt. Express 2019, 27, 7560.
- [33] C. To, T. L. Hellebrekers, Y.-L. Park, presented at Intelligent Robots and Systems (IROS), Hamburg, Germany, September 2015.
- [34] B. H. Lee, Y. H. Kim, K. S. Park, J. B. Eom, M. J. Kim, B. S. Rho, H. Y. Choi, *Sensors* 2012, 12, 2467.
- [35] M. Campbell, P. Singh, K. Kate, C. K. Harnett, MRS Adv. 2019, 4, 1341.
- [36] H. K. Graham, J. C. McConnell, G. Limbert, M. J. Sherratt, *Exp. Dermatol.* 2019, 28, 4.
- [37] C. F. Guimarães, L. Gasperini, A. P. Marques, R. L. Reis, Nat. Rev. Mater. 2020, 5, 351.