

# Adjustable-Stiffness Films via Integrated Thermal Modulation<sup>a</sup>

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We present a new strategy for fabricating thermally responsive adjustable stiffness materials. A microfabricated heater embedded within a composite film is used to modulate the temperature of a low melting point polymer. Currents ranging from 0 to 200 mA were applied

to the microheater and modulated material stiffness  $\approx$ 100-fold between 1.03 GPa and 10.9 MPa. The outside temperature of the composite ranged from 23 to 45.5 °C over this range of currents, suggesting its possible use in biomedical applications. The softened composite was bent into arbitrary shapes and allowed to restiffen, highlighting the reconfigurable nature of the material.



# Introduction

Next generation smart textiles, medical devices, and military applications will require the development of new types of adjustable stiffness materials that are effective at short length scales. Approaches that use temperature, electric fields, and magnetic fields for reversibly modulating material stiffness have been developed.<sup>[1-3]</sup> Fluids actuated by electric (electrorheological, ER) and magnetic (magnetorheological, MR) fields represent the most popular types of adjustable stiffness materials and are created from suspensions of micrometer-sized

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Current address: Biomedical Engineering Institute, South China University of Technology, Guangzhou, 510640, China particles in an insulating fluid that organize into an ordered lattice when exposed to electric and/or magnetic fields, respectively.<sup>[4-6]</sup> During actuation, the apparent viscosity of the ER and MR fluids increases dramatically, resulting in a stiffening effect due to an increase in shear modulus.<sup>[7]</sup> Although microfabricated electromagnets have been demonstrated,<sup>[8,9]</sup> magnetic fields do not scale favorably to microscale dimensions, necessitating very large currents to generate the mT magnetic fields required for fluid actuation. Joule heating is also a significant problem. In contrast, electric fields scale favorably to microscale dimensions, and have been used to actuate ER valves in a microdevice.<sup>[10]</sup> However, the increase in viscosity is limited and these fluids are sensitive to general contaminants like water and always undergo particle settling, potentially affecting actuation repeatability. Thermally actuated materials leveraging the interactions of embedded nanofibers show a 40-fold change in stiffness.<sup>[11]</sup> These materials represent exciting possibilities, but transition times are currently greater than 10 min.

To date, commercial adjustable stiffness materials share three characteristics that in general restrain their use to devices with larger length scales (e.g., structural support) and significant actuation forces (e.g., automotive



<sup>&</sup>lt;sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at http://www.mme-journal.de, or from the author.

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clutches).<sup>[7]</sup> First, these materials require large amounts of external energy to modulate material stiffness. Second, the actuation methods (e.g., electromagnets) are often bulky or impractical for portable use. Third, the physical mechanisms by which stiffness is modulated lose their effectiveness as dimensions shrink, preventing their use in structures at smaller dimensions (millimeters and below). One strategy for creating a more compact adjustable stiffness material is to incorporate microfabricated actuators directly into the material. This approach has been used to create a "smart skin" that acts as a display<sup>[12]</sup> and a surface that can translate and rotate objects placed on it.<sup>[13]</sup> While these approaches result in materials with increased surface functionality,

a) Heater off b) Heater on Force Low Melting Point (MP) High MP Heating

*Figure 1.* An overview of the adjustable stiffness film. (a) At room temperature the inner polymer layer is solid, giving strength to the film. (b) When a current is applied to the internal heater, the middle layer melts and dramatically reduces the strength of the film.

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microfabrication has yet to be used to create materials in which the bulk material properties can be changed. In this paper, we report for the first time a new type of thermally responsive adjustable stiffness material that is actuated via embedded microfabricated resistive heaters. The material consists of laminated sheets, tens to hundreds of micrometers thick, that can be stacked to form sheets of any thickness. Integrating the actuators within the material allows one to achieve a smaller size material than with traditional adjustable stiffness techniques. Small changes in electrical current to the heaters can modulate the stiffness of an embedded low melting point temperature polymer over a very large range ( $\approx$ 100-fold). The advantages of this approach are ease of fabrication, low cost, lowdensity energy requirements, and adaptability to different length scales. In addition, the use of low melting-point (MP) polymers near body temperature opens up the possibility for biomedical applications, such as reconfigurable medical devices or intelligent surgical tools.

# **Experimental Part**

#### **Device Design**

The adjustable stiffness film was made by sandwiching a low-MP temperature material between two higher MP temperature polymers and modulating the temperature of the middle layer. Figure 1 shows an overview. Cantilevers 27.4 mm long, 18.9 mm wide, and  $\approx$ 1.5 mm thick were made from the following materials: polyimide tape (Sigma-Aldrich, thickness: 50  $\mu$ m) as the top layer, a low MP temperature material as the middle layer, and a copper-clad polyimide laminate (Pyralux AP7156E, DuPont) as the bottom layer. Polyimide, a popular material for microfabrication, was chosen for the top and bottom substrate due to its good flexibility and excellent physical and chemical stability. Since adjustable stiffness devices for biomedical applications are our ultimate goal, only



biocompatible materials with low glass transition temperatures ( $T_{\rm g}$ ) or MPs were investigated for the middle layer: Blue Hard Kerr Inlay Wax (Otto Frei, Inc.), MP: 61 °C, nylon 66 (Advanced Industrial, Inc.),  $T_{\rm g}$ : 50 °C, polyurethane (Sigma-Aldrich), MP: 50 °C, polycaprolactone (PCL) (Sigma-Aldrich), MP: 57 °C, and poly(vinyl acetate) (PVAc) (Sigma-Aldrich),  $T_{\rm g}$ : 35 °C. All middle layer films except nylon 66 were prepared via hot-pressing. Nylon 66 was used as received. The cantilever was assembled by putting the polymer films onto the microheater (bottom layer) followed by gently attaching polyimide tape to seal the whole device.

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#### **Fabrication of Microheater**

The bottom polyimide layer containing the integrated heater was fabricated via traditional microfabrication techniques. Doublesided copper-clad polyimide laminate, containing a 9  $\mu$ m thick copper layer on either side of a 50  $\mu$ m thick polyimide film, was first patterned using photolithography, then etched with copper etchant (CE-100, Transene, Inc.) and finally washed with acetone to remove the photoresist (AZ1518). The resulting resistive heater comprised a meandering pattern with a line width of 100  $\mu$ m and interline width of 100  $\mu$ m. The final heater resistance was measured to be 60  $\Omega$ .

#### **Mechanical Force Measurement**

Mechanical force measurements of the cantilevers were performed using a Bose ElectroForce Test Instrument (Bose Corporation, Eden Prairie, MN). Two load cells (250 and 1 000 g) were used for different force ranges (0–2.5 and 2.5–10 N, respectively). Cantilevers were fixed on a stationary platform for testing. A custom-made probe tip was attached to the load cells and used for deflection testing. The cantilevers were characterized by performing two types of measurements: force as a function of displacement over 6 mm, and the change in force of a static cantilever (i.e., no displacement) as current was applied to soften the middle layer.

#### **Differential Scanning Calorimetry**

PCL was found to be the optimal material due to its combination of a low MP and large change in Young's modulus over temperature. In order to quantify the crystallization and melting temperatures of PCL, DSC was carried out with a thermal analyzer (DSCQ100 TA instrument, New Castle, Delaware) under a nitrogen atmosphere. Each sample ( $\approx 10 \text{ mg}$ ) was heated from  $-80 \text{ to} + 100 \degree \text{C}$  at a heating rate of 10 °C · min<sup>-1</sup>. The crystallization and melting temperatures were taken as the top and bottom peaks, respectively.

# **Results and Discussion**

# **Mechanical Characterization**

The adjustable-stiffness cantilever, with PCL as the middle layer, was used to determine the effect of applied current (i.e., internal temperature) on mechanical stiffness. Stiffness was determined by measuring the amount of force required to deflect the cantilever tip 6 mm and then calculating the Young's modulus. Young's modulus, *E*, of a cantilever of length *L* fixed at one end and subject to a point load, *F*, at a distance, *x* (19.6 mm), from the fixed end is given by the equation

$$E = \frac{2F}{ywt^3} (3x^2L - x^3) \tag{1}$$

where y is the vertical displacement of the cantilever, w is the cantilever width (18.9 mm), and t is the cantilever thickness (1.5 mm).<sup>[14]</sup> Figure 2a shows the effect of current on the mechanical stiffness of the cantilever. The cantilever was fixed at one end and the other end was pushed down by the load cell at a rate of 0.02 mm  $\cdot$  s<sup>-1</sup> and withdrawn at a rate of  $0.04 \text{ mm} \cdot \text{s}^{-1}$ . During the movement of the film, a 200 mA current was applied to the microfabricated resistive heater for 60s. Initially (no heating) the force increased linearly with displacement, indicating that the cantilever can be modeled using Equation (1). When current was turned on at t = 68 s, the force first increased quickly and then decreased until the current was terminated at  $t = 128 \, \text{s}$ . The increase in force during the initial heating period can be ascribed to the thermal expansion of residual gas in the PCL thin film, making it temporarily stiffer. The cantilever then lost its stiffness and reached a steady-state stiffness value by the end of the 60s heating window. Once the current was removed, the dropping temperature of the cantilever caused the deflection force to resume increasing as the PCL layer solidified. During probe tip retraction, the measured force on the cantilever quickly went to 0 N, indicating that the cantilever was retaining its deformed shape even when no external perturbing force was present – a key advantage of the adjustable stiffness film as shown in Figure 2a (inset).At the largest displacement (6 mm) of the



Figure 2. (a) A representative mechanical characterization of a 1.5-mm-thick PCL-based adjustable stiffness film using the electroforce system and load cell: (top) force measured during the testing procedure; (middle) displacement of the sensing probe; (bottom) amount of current applied to the microheater over time. (b) The steady-state deflection force, measured at a constant displacement, depended on the current amplitude. (Top) change in steady-state deflection force; (middle) transient and then constant displacement of the sensing probe; (bottom) current applied to the microheater; (c) the steady-state Young's modulus of the film was characterized over a range of currents. Above 120 mA, the Young's modulus is independent of the applied current.



cantilever, the measured force with no current was 9.44 N, corresponding to a Young's modulus of 1.03 GPa. In contrast, the measured force after 60 s of heating was 0.10 N, or a Young's modulus of 10.9 MPa. Thus, the stiffness of the cantilever after applying a 200 mA current for 60 s was approximately 1.1%, or 100-fold less than, the stiffness at room temperature.

In addition to PCL, other polymers were tested as middle layers for the cantilever such as wax, nylon 66, waterborne polyurethane (WPU) and PVAc. Experimental results are shown in the Supporting Information (Figure S1–S4). The ratio of the film stiffness with and without applying a 200 mA current for 60 s was calculated as 2.3% for wax, 31.0% for nylon, 47.8% for WPU, and 10.2% for PVAc. These results confirm that PCL is the best material with the largest change in stiffness among the low MP temperature polymers that we tested.

The steady-state deflection force depended on the current amplitude, as shown in Figure 2b. The experimental protocol was divided into two steps: the cantilever was first deflected from 0 to 4 mm at a rate of 0.02 mm  $\cdot$  s<sup>-1</sup>, followed by quiescence at 4 mm for 800 s. The deflection force was found to increase with the bending of the cantilever until its displacement was 4 mm. An extra 200 s was allowed for the cantilever to reach equilibrium at room temperature before applying a current. A series of currents were then applied to the cantilever and the change in force versus time was recorded for each. For currents greater than 120 mA, the final steady-state deflection force was always  $\approx 0.1 \text{ N}$ , regardless of initial deflection distance (see Figure S5 in the Supporting Information). The force required to deflect the cantilever was always independent of the current used for heating, as long as the generated heat could fully melt the middle layer. As current amplitude increased, the time to achieve the steady-state deflection force of  $\approx\!0.1\,N$ decreased. At currents below 120 mA the steady-state deflection force, and thus Young's modulus, was a function of the current amplitude, as shown in Figure 2c. The final deflection forces for the currents of 50, 100, and 120 mA were 5.1, 2.7 and 0.1 N, respectively. These data indicate that the stiffness of the cantilever could be adjusted to any values within the range of 10.9 MPa-1.03 GPa using currents ranging from 0 to 120 mA. Fitting a curve to the data points in Figure 2c yields the equation

$$E = 1.08 - 0.035 e^{I/35} \quad (0 \le I \le 120 \text{ mA})$$
(2)

where I is the applied current and E is the steady-state Young's modulus (in GPa) of the cantilever. Currents larger than 120 mA can shorten the time needed to change the stiffness but always yield a final Young's modulus of 10.9 MPa. Thus, there is a tradeoff between the rate of stiffness change and control over the degree of steadystate stiffness.

The adjustable stiffness cantilevers we used were about the size of a postage stamp (Figure 3a), but different sizes, up to the size of a conference poster or larger, could be made. We fabricated small constructs 7 cm long and 7 mm wide and used them to demonstrate how the material can be molded into arbitrary shapes (Figure 3b,c). Current was applied to the constructs which were then held in particular shapes. We have not quantified the minimum bending radius of the material, however, a flat sample can easily be recovered from the shapes shown in Figure 3b and c. Turning the current off caused the middle layer to solidify and retain the new shape. The material is easily bent into multiple shapes using one's hands. The construct does not become too hot to handle even after 200 mA of current for 60 s, as shown by the temperatures in Table 1. Polyimide is a good thermal insulator, which minimizes the amount of heat escaping from the material. In ambient environmental conditions, the construct took about 45-50s to totally soften with a current of 200 mA. Once it was fashioned into a new geometry, the construct took about 200 s to restiffen and hold its shape. These rapid response times are a result of the microscale lengths involved. The thin PCL layer in intimate contact with the resistive heaters ensures that the material will rapidly heat up, while the large surface area to volume ratio of the material allows rapid cooling. Even though the middle layer is changed to a highly viscous fluid upon melting, the thickness of the construct stayed approximately uniform (i.e., reflow of the PCL within the construct was minimal).

# **Thermal Characterization**

The outside temperature of the cantilever is determined by the amount of Joule heating within the micropatterned resistive heater. As the current increases, Joule heating



Figure 3. (a) The film used for mechanical characterization was slightly larger than the US postage stamp. (b) This film can be fashioned into arbitrary shapes. (c) A slightly longer film was used to make closed arbitrary shapes. A 200 mA current was briefly applied to soften the film, which was then fashioned into a new shape. After cooling, the films held their shape indefinitely. Scale bars in all images represent 1 cm.



*Table 1.* The top and bottom film temperatures were measured after heating for 60 s at several current levels. The temperature gradient within the film increases as the current increases due to changing PCL properties and the temperature gradient with respect to the environment.

Current	Top temperature °C	Bottom temperature °C	C Temperature difference
100 mA	26.30	30.95	4.65
150 mA	31.62	39.00	7.38
200 mA	36.38	45.51	9.13

raises the cantilever temperature. At the same time, the rate of heat flow out of the cantilever also increases because of the increased temperature gradient with respect to the environment. Eventually, the cantilever reaches a steady-state

temperature once heat flow out of the cantilever equals the amount of heat generated by the resistive heater. Evidence of the steady-state temperature is shown by the constant deflection forces in Figure 2b. The cantilever temperature was measured by attaching surfacemount thermistors to its top and bottom surfaces. Figure 4 shows the top and bottom surface temperatures before and after heating at 200 mA for 60 s. The bottom surface, which contains the microfabricated heater, registered an immediate temperature increase when the current was switched on, while the top surface temperature showed a delay of several seconds before its temperature increased. The temperature delay was a result of the delayed heat flux through the middle (PCL) layer. At 60s, the top and bottom surface temperatures were 36.4 and 45.5 °C. After switching the current off, both temperatures briefly continued to increase before decreasing. The top layer showed a delayed temperature drop compared to the bottom layer. The effects of different current amplitudes on cantilever temperature were also tested and are summarized in Table 1. The temperature difference between the top and bottom surfaces became larger at as currents increased, which suggests that the thermal conductivity of the PCL is a function of temperature and decreases when the temperature of the cantilever rises.

A 3D finite element model of the cantilever was simulated using COMSOL

multiphysics software. The temperature change of the cantilever with a 200 mA current was modeled. All the parameters except thermal conductivity of PCL were found in earlier publications (see Supporting Information). Based



*Figure 4.* (a) Surface temperature measurements were made of the PCL-based adjustable stiffness film (top), while a 200 mA current for 60 s (bottom). (b) The surface temperature of the film was simulated using COMSOL. The modeling results agreed with the experimental measurements.

on the measurements in Table 1, the average value of the thermal conductivity of the middle PCL layer was assumed to be 0.08 instead of  $0.18 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  measured at room temperature.<sup>[15]</sup> After running the simulation for 60 s, the top and bottom surface temperatures were 36.18 and 45.06 °C, respectively, which are in good agreement with our measurements (top: 36.38 °C, bottom: 45.51 °C).

We were also interested in the mechanical properties of the cantilever at different constant temperatures, especially around 37 °C considering its possible biomedical applications. Experiments were conducted in which the temperature of the cantilever was set to a specific value and allowed to equilibrate with the environment for 30 min. The cantilever was then displaced 2 mm. Manual adjustment of the current source and visual inspection of the measured temperature on the top surface ensured that a constant temperature was maintained during testing. Figure 5 shows the force measurements on the device in the temperature range of 23–45 °C. When the device was heated above room temperature, the deflection force remained constant at 3.3 N until the temperature reached pprox37 °C. Thereafter, the deflection force rapidly decreased between 37 and 40 °C, and eventually reached a minimum force of 0.1  ${\rm \tiny N}$  at 45  $^{\circ}\text{C}.$  This dramatic change in stiffness over a temperature difference of 3 °C highlights that only a small amount of heat is needed to reduce stiffness if used inside the human body. As the temperature was decreased from 45 °C, the deflection force stayed approximately constant until the temperature was lower than 34 °C, resulting in a stiffening hysteresis effect, as shown in Figure 5. DSC was used to determine the melting and recrystallization points



Figure 5. The force required to deflect the cantilever a distance of 2 mm was measured over a range of temperatures. Temperatures were measured on the top surface of the film, furthest away from the integrated heater. Softening the film requires a higher temperature than solidifying it. This hysteresis effect was confirmed via a DSC scan of pure PCL (inset).

of pure PCL polymer (Figure 5, inset): 57 and 39 °C, respectively. Thus, a lower temperature is needed for nucleation, and subsequent restiffening, of PCL compared to melting. Two strategies could be used to minimize the hysteresis. One is to prepare PCL polymers that contain nanoparticles. The addition of nanoparticles as nucleating agents can facilitate the formation of PCL crystals at higher temperature and thus shorten the temperature difference between the melting and recrystallization process.<sup>[16]</sup> The other method is to bathe the PCL with a cool liquid or stream of air, thus rapidly reducing its temperature below the recrystallization point.

# Conclusion

We describe, in this paper, a new strategy for fabricating adjustable stiffness materials composed of a low MP temperature polymer and an integrated microheater. Materials made using this approach are thin, require minimal power, and can be manufactured in large quantities at low cost. The material can be tailored to different applications by using polymers with different MPs for the middle layer and by stacking multiple adjustable stiffness sheets to form thicker composites. We believe adjustable stiffness materials made using this approach will enable new applications, including (i) smart surgical tools that adjust their stiffness based on tissue type; (ii) medical devices that can conform to patientspecific anatomy; (iii) reconfigurable textiles for body protection (e.g., knee or arm pads); (iv) reconfigurable displays via the use of transparent polymers and resistive heaters; (v) temporary structural support, such as holding a tool or machine part during manufacturing; (vi) reconfigurable rudders, fins, or wings for next generation underwater vehicles or airplanes. The layered thermal approach to adjustable stiffness materials has a couple of drawbacks. Reflow of the melted middle layer could be a problem depending on its viscosity, which could lead to non-uniform material thickness. We observed this phenomenon when using wax as the middle layer. Also, there is a tradeoff between the material strength during its off-current state and the transition speed. Transition speed (from hard to soft or vice versa) increases as the middle layer thickness is decreased, but the thinner middle layer decreases material strength. For applications that require a high strength material and fast transition times, multiple stacked layers could be a reasonable solution.

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- S. Kiyonaka, K. Sugiyasu, S. Shinkai, I. Hamachi, J. Am. Chem. Soc. 2002, 124, 10954.
- [2] H. Singh, M. Wang, G. C. Rutledge, T. A. Hatton, Adv. Funct. Mater. 2008, 18, 462.
- [3] M. S. Cho, H. J. Choi, K. W. To, Macromol. Rapid Comm. 1998, 19, 271.
- [4] T. Hao, Adv. Colloid Interface 2002, 97, 1.

- [5] K. H. Song, B. J. Park, H. J. Choi, *IEEE Trans. Magn.* 2009, 45, 4045.
- [6] T. C. Halsey, Science 1992, 258, 761.
- [7] J. Wang, G. Meng, J. Mater. Des. Appl. 2001, 215, 165.
- [8] A. C. Siegel, S. S. Shevkoplyas, D. B. Weibel, D. A. Bruzewicz, A. W. Martinez, G. M. Whitesides, Angew. Chem. 2006, 45, 6877.
- [9] H. Lee, M. Purdon, R. M. Westervelt, Appl. Phys. Lett. 2004, 85, 1063.
- [10] X. Z. Niu, W. J. Wen, Y. K. Lee, Appl. Phys. Lett. 2005, 87, 243501.
- [11] J. R. Capadona, K. Shanmuganathan, D. J. Tyler, S. J. Rowan, C. Weder, *Science* **2008**, *319*, 1370.
- [12] A. Richter, G. Paschew, Adv. Mater. 2008, 20, 1.
- [13] J. W. Suh, R. B. Darling, K. F. Böhringer, B. R. Donald, H. Baltes, G. T. A. Kovacs, J. Microelectromech. Syst. 1999, 8, 483.
- [14] G. T. A. Kovacs, "Micromachined Transducers Sourcebook", WCB/McGraw-Hill, Boston 1998.
- [15] Y. Agari, A. Ueda, J. Polym. Sci., Part B: Polym. Phys. 1994, 32, 59.
- [16] T. Dong, Y. He, B. Zhu, K. M. Shin, Y. Inoue, *Macromolecules* 2005, 38, 7736.

