

Stepped Moduli in Layered Composites

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This paper describes adaptive composites that respond to mechanical stimuli by changing their Young's modulus. These composites are fabricated by combining a shorter layer of elastic material (e.g., latex) and a longer layer of stiffer material (e.g., polyethylene and Kevlar), and fixing them together at their ends. Tension along the layered composite increases its length, and as the strain increases, the composite changes the load-bearing layer from the elastic to the stiff material. The result is a step in the Young's modulus of the composite. The characteristics of the step (or steps) can be engineered by changing the constituent materials, the number of layers, and their geometries (e.g., sinusoidal, hierarchical, two-dimensional web-like, rod-coil, embedded, and ring structures). For composites with more than two steps in modulus, the materials within the composites can be layered in a hierarchical structure to fit within a smaller volume, without sacrificing performance. These composites can also be used to make structures with tunable, stepped compressive moduli. An adaptation of these principles can generate an electronic sensor that can monitor the applied compressive strain. Increasing or decreasing the strain closes or opens a circuit and reversibly activates a light-emitting diode.

1. Introduction

Most materials have mechanical properties that do not adapt in response to stimuli (e.g., stress, strain, environmental conditions, and patterns of use) over wide ranges of strain. The elastic deformation of a conventional structural material or composite shows an approximately constant Young's modulus: the stress increases linearly as a function of strain, until the material undergoes plastic deformation or fails.^[1,2] These circumstance-invariant mechanical properties make engineering design simpler, but constrain the capability and use of these materials. For example, metals are stiff materials with high Young's modulus, but can fail by fatigue at low strain; elastomers have low Young's modulus and high elongation-at-break (the strain at which the material breaks), but deform irreversibly and break at low stress.

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Circumstance-adaptive materials (CAMs) are those that can change their properties—mechanical, optical, electrical, magnetic, biological, and so on—to respond to their use or environment;^[3–8] they represent a current challenge in materials science. Among the wide variety of possible CAMs, we focus on materials whose mechanical properties change in response to their circumstance. We use the word “circumstance” intentionally for its breadth: we wish to consider a range of factors that characterize the environment, including temperature, water content, strength of electric or magnetic fields, patterns and history of use, and others (as appropriate).

There are different types of stimuli that can induce changes in mechanical properties of materials. As an example of CAMs in Nature, sea cucumbers rapidly change their stiffness in the face of danger by controlling the interactions among the collagen fibers by secreting chemicals into their dermis.^[9–12] Inspired by this

mechanism, composites of cellulose fibers or nanocrystals dispersed in polymers have been fabricated to show a reversible reduction of tensile modulus upon exposure to physiological conditions.^[13–16] Coiled fibers and braids that change porosity in response to temperature showed an increase in modulus and tensile actuation.^[17] Electrical potential provides another simple way to manipulate mechanical properties. Oxidative and reductive potentials change the cross-linking capacity of ions within a gel-like matrix,^[18] and electrical current induces phase transition (solid to liquid) by Joule heating.^[19] Magnetorheological fluids and elastomers exhibit tunable elastic stiffness in response to an external magnetic field.^[20,21]

Mechanical stress can also serve as a stimulus to change mechanical properties of materials. Liquid crystals^[22] or carbon nanotubes^[23] embedded in elastomers show a permanent self-stiffening response when subjected to recurring elastic stress; this response is superficially similar (although based on an entirely different mechanism) to the adaptive strengthening of bones that improves their strength due to repeated mechanical loading.^[24] A few crystalline solids (Fe₃C and Al₃BC₃)^[25] and physically associating synthetic polymer networks^[26,27] also change their mechanical strength in response to mechanical stimuli. This change is, however, different from the self-stiffening behavior of liquid crystals in elastomers, as these materials have an increasing modulus with applied strain (called strain stiffening), and the change is reversible. Collagenous biomaterials such as mammalian skin, arteries, ligaments and tendons are also strain-stiffening.^[28,29] This nonlinear

behavior is attributed to the crimped geometrical arrangement of the collagen fibers in elastin matrix; the collagen fibers must unfold before stretching upon tensile strain. The stiffness of the material increases as failure approaches and limits excessive extension to prevent mechanical failure (e.g., a tear of the skin).

Biological systems provide examples and inspiration for new types of CAMs, but usually require complex mechanisms that are difficult to replicate synthetically. For example, modification of bone requires dissolution (by osteoclasts) and deposition (by osteoblasts) of materials, and is slow and dissipative.^[24] No synthetic system has reached this level of complexity because such systems are limited by the properties of their constituent materials, by the desire to have properties that can be used reliably in engineered systems, and by the difficulty in designing truly dissipative structures in which material is added or subtracted by transport and local chemistry. The collagenous biomaterials, however, suggest a simple architectural strategy to fabricate synthetic, strain stiffening materials as composites by combining a crimped stiff material with an elastic material. Mathematical analysis shows that strain stiffening is beneficial for improving the fault tolerance of structural materials.^[30–32]

We wish to explore the range of mechanical properties that can be built into a new type of CAMs (especially, here, composite materials) using combinations of components with very different mechanical properties, and with unfamiliar physical architectures inspired by the structures of collagenous materials. At this point, these studies are more designed to explore the range of circumstance-adaptive properties that can be produced than to solve a specific problem in an engineered system.

The objective of this work was to design and fabricate CAMs that have tunable strain-stiffening properties. We sought to fabricate the materials as composites in which the Young's modulus changed in discrete steps, according to design, with applied strain. We prepared these materials by layering sheets (fabrics and polymers) of different lengths and mechanical strengths to produce a composite with multiple Young's moduli; we call this system a "stepped-modulus composite". In the examples given here, the composites are composed of a longer sheet of material that is stiff under tensile stress (e.g., polyethylene, aramid fabric (Kevlar)) and a shorter sheet of an elastic material (e.g., latex); these sheets are fixed with an adhesive at their ends, but have a section in the center that is not attached (Figure 1A). Increasing the strain initially stretches the shorter, elastic material but at a strain set by the difference in length of the shorter and longer materials, shifts the stress-limiting component of these composites from the elastic material to the stiff material. Thus, at low strains, the elastic material dominates the mechanical properties of the composite. When strain on the composite is such that its length equals the length of the stiffer material, the mechanical properties of the stiffer material largely dominate these mechanical properties of the composite. Combining multiple layers of fabrics and polymers with increasing Young's moduli and increasing lengths offers a readily applied strategy for the fabrication of composites in which it is possible to engineer mechanical properties to show multiple steps with different stress-strain characteristics.

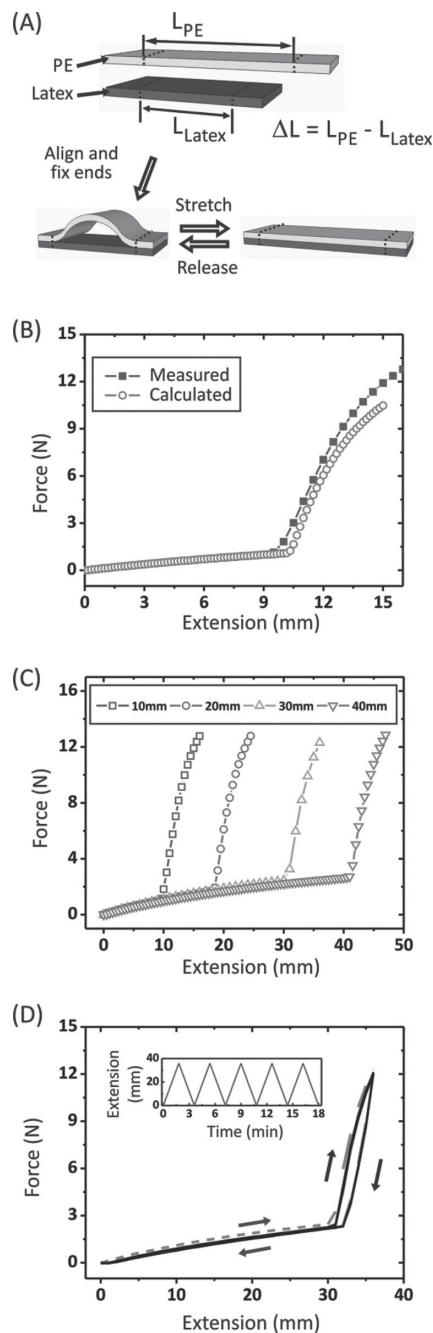


Figure 1. A) Schematic of a stepped modulus composite of latex and PE. Two strips of latex and PE, with the same width but differences in length (ΔL), were aligned and attached at both ends. As strain was applied in tension, the latex strip elongated and the wavy PE strip straightened. B) The measured and calculated force-extension plots showed two steps as the composites of latex and PE elongated. The modulus increased rapidly when the extension was equal to ΔL (10 mm) since the Young's modulus of PE is much larger than latex. C) The ΔL varied from 10 mm to 40 mm and showed good agreement with the threshold extension (10, 20, 30, and 40 mm from left to right). D) Force-extension plot for cyclical testing of the latex-PE composites. The dotted line represents the first cycle and the arrows show the ascending and descending strain. The ΔL for this composite was 30 mm, the maximum extension was 36 mm and the strain rate was 60 mm/min. Inset shows the cyclical extension with time.

2. Results and Discussion

We fabricated the stepped-modulus composites by combining two or more layers of Kevlar, polyethylene (PE) and latex. The Young's moduli of those materials are different by orders of magnitude (10–100 MPa for latex, 110–450 MPa for PE, and 70–110 GPa for Kevlar)^[1,33] and make it possible to design CAMs exhibiting discrete levels of tensile strength over a wide range of strain and stress. The moduli of latex (2.7 MPa), PE (55 MPa) and Kevlar (24 GPa) that we measured showed lower values than those reported in literature (which can be attributed to the different grades of materials), but still showed differences of orders of magnitude (Supporting Information, Figure S1).

2.1. Composites with Two Steps in Modulus

We fabricated stepped-modulus composites with two levels of Young's modulus by aligning the ends of a shorter elastic layer made of latex with the ends of a longer stiff layer made of PE (Figure 1(A)) and gluing them together (PE-latex composites). The composites can be fabricated by first pre-stretching the shorter elastic layer and then assembly with the longer stiff layer, for example, the recently reported graphene-elastomer laminates do to control the crumpling of the graphene film.^[34] The layers can be fixed in several different ways depending on the surface properties of the components and the desired properties; examples include different types of adhesives, permanent heat-sealing, sewing, and reversible mechanical connectors by magnetic or electric fields.

Figure 1B summarizes the mechanical properties of the PE-latex composites measured using a conventional tensile tester. We plot force as a function of extension, rather than relative strain, for easy comparison of the length difference of components with the threshold extension of the stepped-modulus composites by using the same unit (mm). For extensions smaller than the difference of the two layers in length (ΔL), which was 10 mm, the Young's modulus of the composite depended upon the modulus of the latex strip. For extensions greater than ΔL , the modulus of the PE strip determined the modulus of the composite (the modulus of the latex was negligibly small compared to that of PE). We excluded the glued ends of strips when we defined their lengths (L_{PE} and L_{Latex}) and calculated their difference in length (ΔL) since the ends were gripped by the tensile tester and were not in tension during the measurement. To see how each strip affects the mechanical strength of the composite, we calculated the force to stretch the PE-latex composite by using the force values required to stretch the single PE and latex strips in Supporting Information Figure S1:

$$F(x) = \begin{cases} F_{Latex}, & 0 < x < L_{PE} - L_{Latex} \\ F_{Latex} + F_{PE}, & L_{PE} - L_{Latex} \leq x \end{cases} \quad (1)$$

In these equations, x is the extension and $F(x)$ is the calculated force to stretch the PE-latex composite. F_{Latex} is the force to stretch the single latex strip, and F_{PE} is the force to stretch the single PE strip.

We intentionally use force values instead of stress for easy comparison of calculated values with the measured ones; the

sum of stress values of each component of a composite is not equal to the stress values of the composite as shown in Equation 2:

$$\sigma(x) = \frac{F(x)}{A_{Latex} + A_{PE}} = \frac{F_{Latex} + F_{PE}}{A_{Latex} + A_{PE}} \neq \frac{F_{Latex}}{A_{Latex}} + \frac{F_{PE}}{A_{PE}} = \sigma_{Latex} + \sigma_{PE} \quad (2)$$

Here, $\sigma(x)$ is the stress of the composite, σ_{Latex} is the stress of latex, and σ_{PE} is the stress of PE in tension. A_{Latex} is the cross sectional area (width \times thickness) of latex, and A_{PE} is the cross sectional area of PE. The steps in modulus of the composite, however, should be distinguished from the steps in force. For example, if the composite in Figure 1 consists entirely of latex layers with the same structure (i.e., latex-latex composite), it would show an increase in force when the extension exceeds ΔL , but the modulus remains constant.

The threshold extension where a step in mechanical properties occurs depends entirely on the ΔL between latex and PE. Tuning these properties to change the mechanical characteristics of the composites is straightforward. When the ΔL between the PE and latex layers changed from 10 to 40 mm, the threshold extension shifted accordingly (Figure 1C). We performed a cyclical test on the stepped-modulus composite with ΔL of 30 mm by applying a triangle-wave strain for five cycles to measure the reproducibility of the changes in mechanical strength. The composites showed reversible two-stepped modulus with little hysteresis (Figure 1D).

The latex layer of the composite enabled the reversible changes in modulus, since the stored elastic energy of the latex, when it is elongated, provided a restoring force for the composite to recover its initial length when the tensile strain was released. Moreover, the latex layer had elongation-at-break (the strain at which the material breaks) higher than the ΔL , thus prevented the composite from breaking. Layered composites composed entirely of elastic materials can maximize these advantages on reversibility. For example, we fabricated a stepped-modulus composite using only elastomeric materials (thermoplastic urethane (TPU) and a silicone-based elastomer, Ecoflex) and it also showed two discrete levels of mechanical strength (Supporting Information, Figure S2). Contrary to the composites of elastomeric materials, composites of stiff materials that had elongation-at-break lower than the ΔL showed irreversible, pulse-like force-extension profiles. We fabricated a composite by combining four layers of aluminum with different lengths on a short latex layer. The force-extension plot showed four sharp peaks at the threshold extensions of each aluminum layer since the aluminum layers break at low strain (Supporting Information, Figure S3). The examples show that the mechanical properties of the composites can be engineered to show a range of properties by selecting the constituent materials, and by choosing the geometries with which they are combined.

2.2. Composites with Three Steps in Modulus

We also fabricated stepped-modulus composites with three steps in modulus using layers of latex, PE, and Kevlar to demonstrate composites with several levels of mechanical strength.

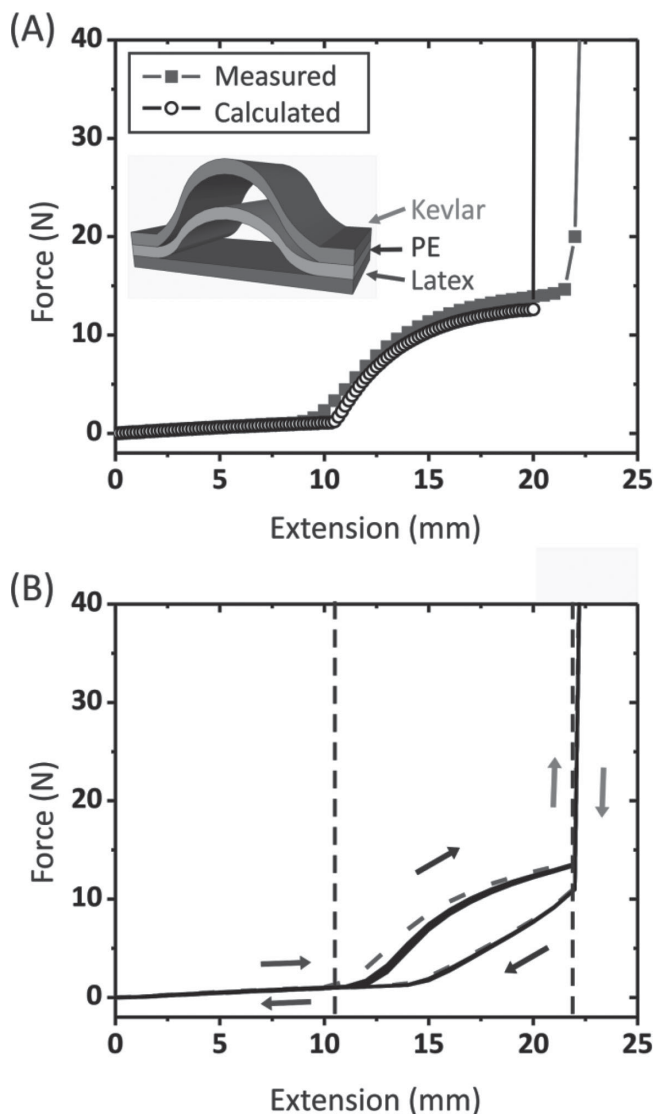


Figure 2. A) The force-extension plot for the stepped-modulus composites composed of latex, PE and Kevlar sheets showed three levels. The layers were combined by increasing stiffness and length: the elastic latex was the shortest, the stiffer PE was longer ($\Delta L = 10$ mm) and the stiffest Kevlar was the longest ($\Delta L = 20$ mm). Up to 10 mm of extension, the modulus of the composite depended on latex, then the modulus increased once the PE sheet started to bear force (approx. 10–22 mm of extension). After exceeding 22 mm of extension, the modulus increased again as the Kevlar fabric dominated the modulus of the composite. B) Force-extension plot for cyclical testing of the Kevlar-PE-latex composite. The maximum extension was 23 mm and the strain rate was 60 mm/min. The dotted vertical lines show two threshold extensions, 10 and 22 mm. The arrows represent the direction of the measurement.

We combined the materials in increasing stiffness and lengths; the elastic latex layer was the shortest (30 mm (W) \times 90 mm (L)), the stiffer PE layer was 10 mm longer than the latex (30 mm (W) \times 100 mm (L), $L_{PE} - L_{Latex} = 10$ mm), and the stiff Kevlar layer was 20 mm longer than the latex (30 mm (W) \times 110 mm (L), $L_{Kevlar} - L_{Latex} = 20$ mm) (Figure 2A inset). The stepped-modulus composite showed three discrete steps in

mechanical strength when elongated (Figure 2A) and was consistent with calculations in the following Equation (3):

$$F(x) = \begin{cases} F_{Latex}, & 0 < x < L_{PE} - L_{Latex} \\ F_{Latex} + F_{PE}, & L_{PE} - L_{Latex} \leq x < L_{Kevlar} - L_{Latex} \\ F_{Latex} + F_{PE} + F_{Kevlar}, & L_{Kevlar} - L_{Latex} \leq x \end{cases} \quad (3)$$

This stepped-modulus composite also showed reversible changes of mechanical strength under cyclical loading (Figure 2B).

2.3. Other geometries of Stepped Modulus Composites

By layering fabrics or polymers, we demonstrated stepped-modulus composites with two and three levels of Young's modulus as a proof of concept. The mechanical characteristics of the stepped-modulus composites are not limited to the geometries used in the aforementioned composites, but different geometries can be designed to accommodate specific physical requirements. For example, we fabricated smaller sizes of the stepped-modulus composite that occupy less volume and can be integrated more effectively into devices and fabrics, while maintaining their unique mechanical behavior. Figure 3A shows four different configurations of the PE-latex composite fabricated by fixing the PE layer to the latex layer in a sinusoidal fashion. We confirmed numerically that the amplitude of the curved PE layer decreases along with the wavelength as the number of attachment increases while maintaining the total arc length (Supporting Information, Figure S4). When stretched, the composites with two, three and four waves (zero, one, two and three attached lines between the PE and the latex layer) showed negligible difference in performance (Figure 3B). Further numerical analysis for the shape and dimensions of the sinusoidal configuration is possible by using the theory for delamination blisters.^[35]

The stepped-modulus composites with sinusoidal configuration do not require uniform amplitude through their length, and the number of steps in modulus depends only on the numbers of constituent materials. To demonstrate, we fabricated a PE-latex composite which has three different amplitudes at each section (defined by points of attachment) and stretched it in tension. The measured force of the composite showed two steps regardless of the non-uniform amplitude of the PE layer since the stiff layer (e.g., PE) started to elongate only when the elastic layer (e.g., latex) fully stretched to the length of the stiff layer (Supporting Information, Figure S5).

The wavelength of the composites with sinusoidal configuration also does not affect the number of steps in modulus. When the wavelength of the PE layer changed through the width as well as the length of the composite, the number of steps in tensional modulus still depended on the number of constituent materials (Supporting Information, Figure S6). The composite, however, distorted its shape as the amount of extension was not uniform through the width.

To decrease the volume occupied by stepped-modulus composites of Kevlar, PE, and latex, we utilized multiple generations of hierarchical structure (Figure 3C). Hierarchical structures have been shown outstanding mechanical performance

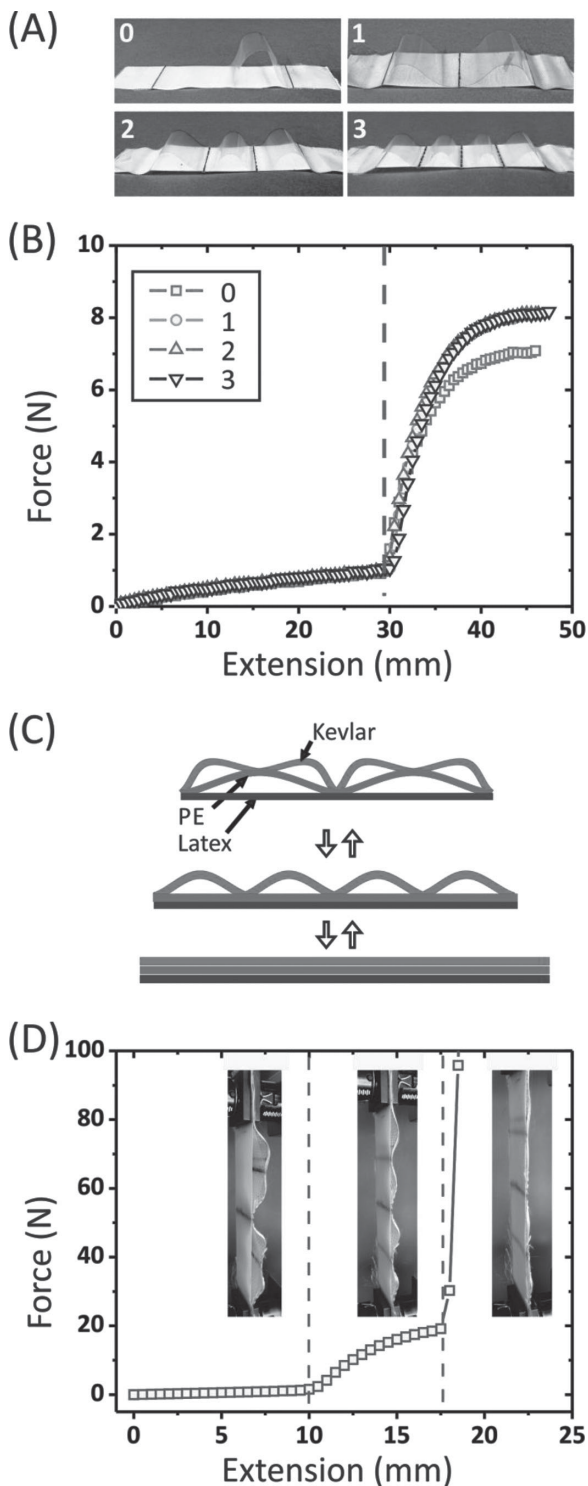


Figure 3. A) Four configurations of PE-latex composites with increasing number of attachments, but the same total PE arc length. Inset numbers represent the number of attachments in each composite (excluding attachments at the ends). B) The force-extension data for the four composites. All configurations showed similar performance. The ΔL is 30 mm for all configurations. C) Schematic of a Kevlar-PE-latex stepped-modulus composite in three different states. Three layers of the composite are hierarchically structured and change their configuration depending on the amount of strain. D) Force-extension plot of the Kevlar-PE-latex composite. Insets are the photos of the composite at each state.

and efficiency in biological materials and artificial structures.^[36] The composition of the Kevlar-PE-latex composite was the same as the stepped-modulus composites shown in Figure 2: a long Kevlar strip, a PE strip, and a short strip of latex. As the strain increased, the mechanical properties were determined first by the latex, then the PE, and last by the Kevlar. The measurement of the force confirmed that the hierarchical configuration showed the characteristic mechanical properties of a stepped-modulus composite with three levels of tensile modulus (Figure 3D).

The geometries of stepped modulus composites are not limited to one-dimensional structures and can be designed to respond to mechanical stimuli in different directions. To demonstrate an example of two-dimensional stepped modulus composites, we fabricated a PE-latex composite with an octagonal web-like configuration (Figure 4A). The composite consisted of a web of latex and strips of PE attached along the eight radial lines of the web. When tension was applied by lifting the center of the composite while the ends of the radial lines were fixed to the substrate, the composite showed an increase in modulus at ≈ 35 mm of elevation (Figure 4B). When compared to a web of latex alone, the PE-latex composite withstood the same stress at much lower strain (approximately 5 N at 50 mm vs 170 mm of elevation). A web of

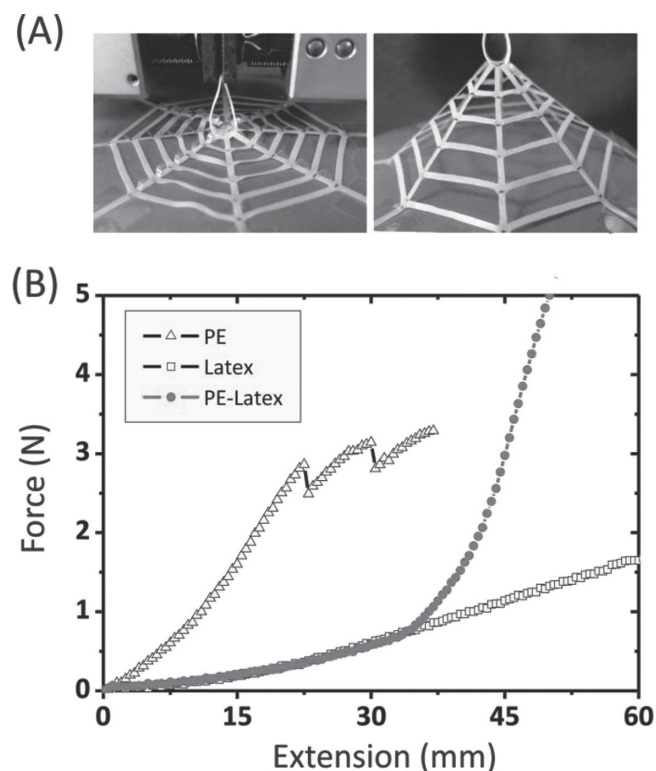


Figure 4. A) Photographs of a PE-latex layered composite with an octagonal, web-like configuration at rest (left) and in tension (right). At rest, the long diagonal of the latex octagonal web is 91 mm and the length of PE layer attached along the four diagonal lines is 113 mm. The width of each segment is 2 mm. The ends of the diagonal segments of the composite were fixed to the substrate and we used a metal wire hooked at the center of the composite to perform the tensile test. B) Force-extension profiles of a single PE (Δ), a single latex (\square) and the PE-latex composite (\bullet) of the same web configuration. The single PE layer began to break at ≈ 20 mm of extension.

single PE layer began to break at lower strain compared to the composite (approximately 20 mm vs 55 mm of elevation). The PE-latex composite prevented physical failure at low strain and severe deformation at high stress. This behavior is analogous to the superior fault tolerance of the web of strain-stiffening spider silks.^[30–32] According to the Pythagorean Theorem, the measured value of threshold elevation is consistent with calculation in the following Equation 4, where L_{PE} is 113 mm and L_{Latex} is 91 mm:

$$h = \sqrt{\left(\frac{L_{PE}}{2}\right)^2 - \left(\frac{L_{Latex}}{2}\right)^2} = 33.5 \text{ mm} \quad (4)$$

Compared to the composites described in Figure 1–3, the PE-latex composite with web configuration showed stepped modulus in a two-dimensional structure in response to strain applied in the perpendicular direction.

The layered composites are distinguished from conventional composites by their discrete steps in moduli as the constituent materials deforms independently without stress transfer between each other. In contrast to the layered composites, the geometries where the deformation of soft component induces stress in stiff components show gradual increase in moduli, which may be desirable in certain applications. To demonstrate, we fabricated a Kevlar-TPU-Ecoflex composite in rod-coil configuration (Supporting Information, Figure S7). As the rod of Ecoflex is elongated, the Kevlar and TPU strips in helical fashion experience shear stress as well as tensile stress. The composite in rod-coil configuration showed gentle increase in modulus, whereas the layered composite of TPU and Ecoflex showed discrete steps in Supporting Information Figure S2.

Embedded structures are another example of the geometries where the deformation of a soft component induces stress in a stiff component. We embedded a composite of Kevlar and TPU in Ecoflex (Supporting Information, Figure S8). The composite shows only two steps in its modulus; these steps can be attributed to the difference between the moduli of TPU and Ecoflex and the modulus of Kevlar (Kevlar (21 GPa) has much higher modulus than TPU (17.7 MPa) and Ecoflex (44 kPa)). We performed finite element analysis to confirm the difference in stress distribution between the embedded and the layered configurations. Figure S8C (Supporting Information) shows the stress is distributed in both of the soft and stiff components of the composite, replicating the structure of the stiff component within the embedded configuration, while the layered configuration shows relatively independent stress distribution in individual components (Figure S8D). The embedded geometries have an advantage; they improve the structural integrity of composites as the stiff component is sequestered inside the soft matrix, however, they also have a limitation since the components can delaminate under strain. The stepped modulus composites have a variety of possible geometries beyond those demonstrated here and can be designed to accommodate desired sizes, shapes and properties such as 1D, 2D, or 3D, and discrete steps or gradual increase.

2.4. Stepped Modulus Composites in Compressive Strain

The composite can also show the stepped modulus in response to other types of mechanical stimuli, such as compressive

strain, when the stimuli are converted to tensile strain. When a material is compressed in one direction, it expands in the transverse direction (Poisson effect) and the expansion can induce tensile strain. As a demonstration of the changes in mechanical strength with compressive strain, we fitted a PE-latex composite around an inflated rubber balloon and measured the mechanical force while compressing the balloon (Figure 5A). As the balloon was compressed vertically, it expanded horizontally and applied tensile strain to the composite. The measured force of the balloon with the composite showed a higher force than a plain balloon with more than 40 mm of compression (Figure 5B). The difference in the force between the two measurements can be attributed to the mechanical strength of PE and rubber and is distributed to the exposed parts of the balloon.

2.5. Application in Electronic Devices

The adaptive properties of a stepped-modulus composite can be extended to other applications that require strain-sensitive properties. The changing shape of a composite, when combined with electric components, could serve to trigger an electric sensor for monitoring body movements. As an example, we demonstrated a prototypical electrical switch (e.g., to sense the stages of extension or compression). The switch consisted of batteries, thin strips of aluminum foil, and an LED. The foil and batteries were attached to the latex layer of a PE-latex stepped-modulus composite and an LED was attached to the PE strip of the composite (Figure 5C). The switch was fitted to a rubber balloon to monitor compressive strain applied in a vertical direction. The compressive strain on the balloon was converted to a tensile strain on the composite, decreased the gap between the latex and the PE layer, closed the electrical circuit, and turned on the LED (Figure 5C, bottom). The combination of an electrical switch with a stepped-modulus composite demonstrates the possibility of converting physical deformation into an electronic signal.

3. Conclusions

We described layered composites with multiple steps in modulus as a new strategy to incorporate different magnitudes of mechanical strength (e.g., ductility and rigidity) into one structure. Unlike most materials that have a constant Young's modulus, these composites show an increase in modulus with applied tensile strain, and thus, have the advantage of strain-stiffening and great versatility in dynamically changing circumstance. The mechanical characteristics of the composites can be engineered with a variety of configurations and compositions by combining different types of materials such as plastics, fabrics, paper, and metal foils, controlling the number of constituent materials, and their relative configurations. Since the composites adapt in response to the applied strain, they could be used as strain sensors and switches. The strain stiffening property of the composites could be used to fabricate new functional constructs, like artificial skin, prostheses, and medical gear, as they resist excessive movements.

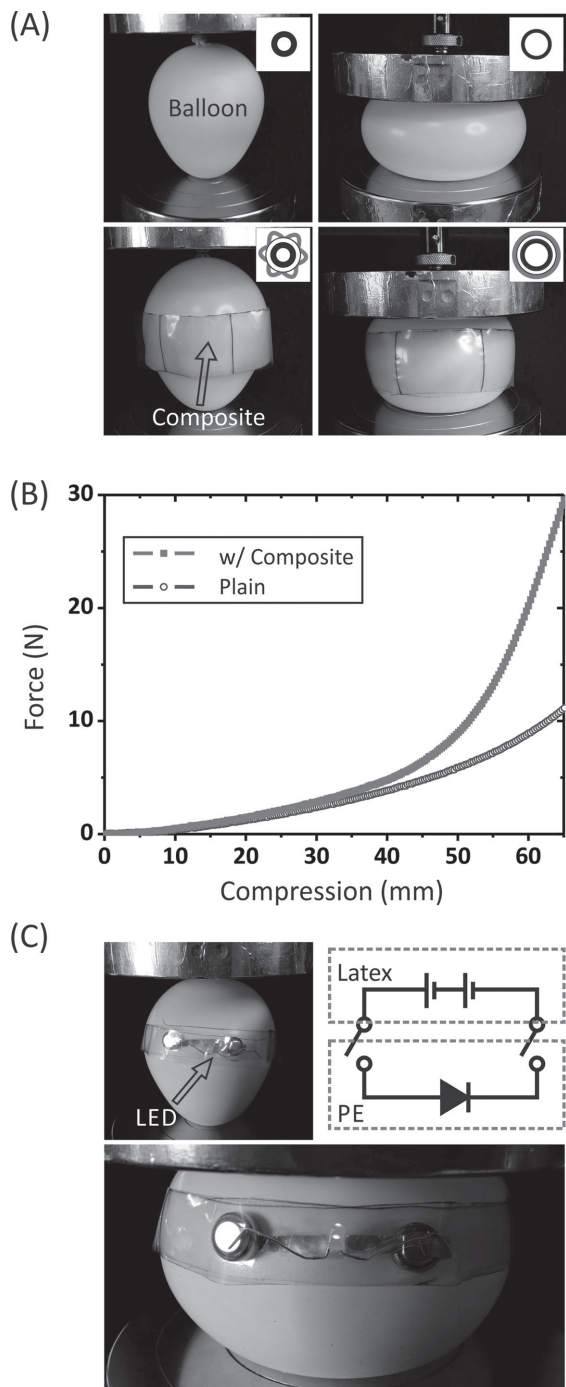


Figure 5. A) Rubber balloons with (bottom) and without (top) a stepped-modulus composite. Compressive strain deformed the balloons and the fitted composite (right). The insets are diagrams to describe the cross sectional shape and approximate size of each state of the samples. The solid annular rings on the top insets represent the plain balloon and the annular rings on the bottom insets represent the balloon (solid), the latex (empty) and the PE (solid) from the center to the perimeter. B) The force-compression plots for the balloon and the balloon with the PE-latex composite showed a difference in force for compression greater than 40 mm. C) An electrical switch for sensing compressive strain. Before applying the strain, the LED was in the off state (top left). Once the strain exceeded a threshold strain, the circuit was closed and the LED turned on. The circuit diagram in the off state is shown on the top right.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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