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# Secondary Reorientation and Hygroscopic Forces in Chitinous Biopolymers and Their Use for Passive and Biochemical Actuation

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**Passive actuation is the production of movement or deformation without external power sources or control systems. This phenomenon has been gaining significant attention in the engineering community due to its potential use in energy-efficient systems, in which part of the functionality is programmed in the material composition to reduce overall cost and complexity. Biological organisms, formed through millennia of evolution in a paradigm of limited resources and energy and at a multiscale equilibrium with their environment, have developed a myriad of outstanding materials and strategies for integrating complex functionalities into their multiscale structural design. In this study, the arthropod exoskeleton's chitinous composition and manufacturing strategies are used to reproduce its complex relations with external forces and water-driven molecular rearrangement and use them to produce electricity and actuate a mechanical hand. The proposed technology is unique in combining the generation of strong forces and the integration of the principles and materials of biological organisms, leading to significant advances in the design and performance of passive solutions integrated into biological systems for a wide range of applications, such as biorobotics, medical devices, and energy harvesting.**

## 1. Introduction

From a mechanical perspective, chitinous cuticles are one of the most extraordinary structures produced by biological systems.[1–3] From mollusk shells' impact resistance, to the tank-like exoskeleton of crustaceans, and the lightweight wings in flying insects, the versatility of chitinous structures is unmatched across biological kingdoms.[4] A fundamental aspect enabling this versatility is the control of chitin organization across all the hierarchical design levels of cuticles.[5] This molecular organization is controlled primarily at the cellular level through the creation of chemical gradients and the polarization of epidermal cells.[6] Chitinous animals have also developed numerous strategies to overcome the inherent limits of their cells in arranging chitinous molecules and have achieved further mechanical enhancements through secondary reorientation. The secondary reorientation of chitinous molecules is driven by strong forces generated from physiological processes, particularly water exchange.[7] Cuticular dehydration and the generation of forces during molting rely partially on mechanisms "programmed" in the material, not on signals from the central nervous system, since these processes have been observed even in amputated sections of the arthropod cuticle.[8]

## 2. Results and Discussion

In this study, we demonstrated that chitinous polymers extracted from arthropod cuticles retained the ability to generate strong hygroscopic forces without external power or control systems. We analyzed the effect of external forces on the material, reproducing some of the mechanical enhancements observed during the molting of the arthropod exoskeleton, and produced similar forces through the response of biomimetic chitinous films to environmental changes for driving mechanical and electrical work (**Figure 1**a).

Chitin, the second most abundant polymer after cellulose on Earth, is part of every ecosystem and is sourceable from multiple organisms or even urban waste.[9,10] In our experiments, we used chitosan (i.e., highly deacetylated chitin) extracted at a deacetylation degree of 87% from shrimp shells (i.e., *Penaeus monodon*), a common byproduct of the fishing industry. The biopolymer was dispersed at a 3% concentration (w:v) in a weak acetic acid solution (1% v:v), a process enabled by the interchain repulsive forces introduced by the protonated amine groups. The chitinous dispersion, which demonstrated the characteristics of a liquid crystal,[11] was spread on a flat surface, and the solvent was allowed to evaporate, resulting in freestanding, water-soluble

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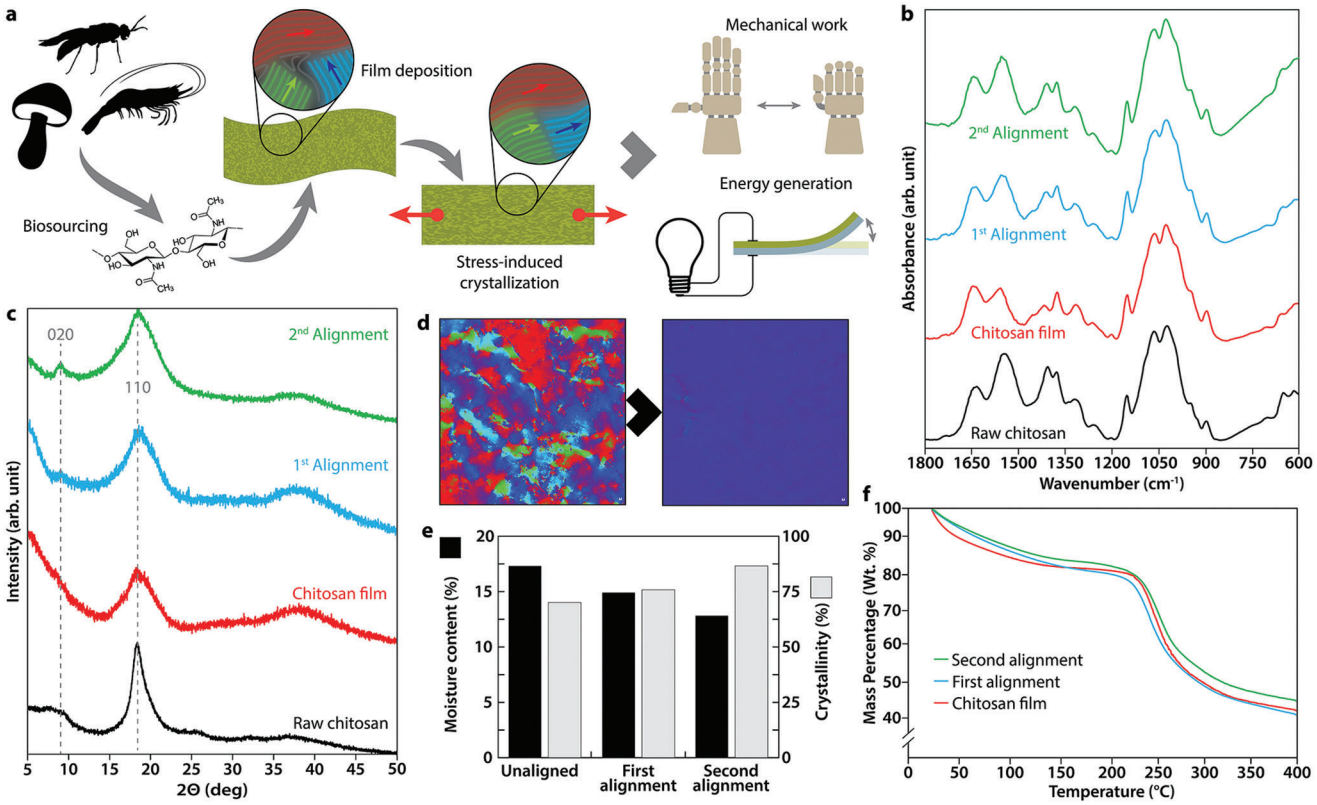



**Figure 1.** Molecular and supramolecular analysis of chitosan films and their dependence on secondary alignment. a) Diagrammatic representation of the production and use of chitinous films for actuation. Chitosan from natural sources was dispersed in solution and cast into films. External forces simultaneously altered the films' molecular organization, water content, and mechanical properties. Conversely, the molecular reorganization of the film due to water exchange resulted in the development of strong forces that drove mechanical and electrical work. b) FTIR fingerprint region for chitosan after its extraction from shrimp shells (black), casting into films (red), the first stretching beyond yield strain (blue, 1st Alignment), and the second stretching beyond yield strain (green, 2nd Alignment). Supplementary Figure 1 show the entire spectrum. c) X-ray diffraction pattern of the films and the raw chitosan. The stress-induced crystallization effect was observed as the relative intensity of the peaks with respect to the amorphous background. The lines in the graph follow the same color code as that for panel b. d) Birefringence map of the chitinous films before and after stretching. Each color represents the main direction of the polymer's slow axis angle and, therefore, the preferred alignment of the area. After stretching, the original alignment domains of the films transformed into a global alignment along the stretching direction. Images correspond to a surface of 2.2 × 2.2 mm. e) Crystallinity and water content of the chitinous films after consecutive stretching. The uniaxial strain resulted in better molecular packing and water removal, which favored closer intermolecular interactions. f) Thermogravimetric analysis of the chitinous films. The lower water content of the unstretched films was reflected in the higher mass loss due to water exchange at 50–150 °C. The samples are color-coded in agreement with the previous panels.

chitinous films of ≈130.5 µm thickness. This thickness is controlled by the volume and concentration of chitosan solutions employed in the casting process. The remaining acetate groups were removed by immersing the chitinous films in a sodium hydroxide solution (4% w:v), thereby forming sodium acetate and giving rise to films of unchanged physical appearance that were insoluble at neutral pH.[12]

To evaluate the molecular and mechanical effects of external forces on the chitinous molecules and to reproduce the secondary alignment of cuticles in arthropods during molting, we stretched the films beyond their yield strength (30 MPa) to their ultimate strain (≈0.27). While reaching the ultimate strain provided the best results, the molecular rearrangement (i.e., stress-induced crystallization) was observed, to a lesser degree, in the whole plastic region of the material. Before stretching, the chitinous films showed an infrared fingerprint (Figure 1b), characterizing an L-2 crystal polymorph[13] with amide I (−CO) and amide II (−NH) bands at 1635 and 1546 $cm^{-1}$, respectively. After stretching, the absorption peaks slightly shifted to higher frequencies (i.e., 1651 and 1560 $cm^{-1}$ for amide I and II, respectively), and the relative intensity of amide II with respect to amide I increased significantly, indicating the formation of more stable amide bonds. Stretching the films also resulted in a significant decrease in the hydroxide (OH) absorption peak at 3100–3600 $cm^{-1}$ (Figure S1, Supporting Information), which was consistent with water loss. This hypothesis was confirmed later in the thermal analyses of the films.

The organizational changes in the chitinous films after stretching were evaluated at higher hierarchical levels. Following stretching, a tightly packed and aligned morphology along the chitosan film's direction of stretching was visible under a Scanning Electron Microscope (SEM) ( Figure S2, Supporting Information). X-ray diffraction (XRD; Figure 1c) confirmed the L-2 crystal polymorph in the unstretched and stretched films previously observed by Fourier transform infrared (FTIR) spectroscopy. However, while the crystal polymorph was the same for


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both films, the orientations of these crystals were not. The different indices of refraction across and along the chitosan molecules allowed us to produce a birefringence map of the films,[14] showing the preferred orientation of the molecules and their association with the alignment domains (Figure 1d). In unstretched films, the orientation domains were characterized by chitosan chains oriented along the same direction, forming a crystal structure that likely originated from the same nucleation point. The immediate observable results after stretching the films were the realignment of the molecules, the disappearance of the crystal domains, and the shift to a uniform alignment along the stress direction for the whole film (Figure 1d). The loss of the (disordered) transition areas between crystal domains also resulted in an increased general crystallinity, from 70% in the unstretched films to 75.8% in the stretched ones. This crystallinity was further enhanced by repeating the stretching process, but repeating the process beyond that point resulted in demising results and minimal enhancements. A second stretching enabled the production of films with 86.6% crystallinity, which was higher than that of the original chitosan from shrimp shells (81.1%; Figure 1c). The stretching strategy reoriented the chitosan chains in the crystalline regions and reorganized in a crystal form and aligned the relaxed chitosan chains in the amorphous regions. The result was an enhanced hydrogen bonding between nearby chitosan chains, more densely packed chitosan crystals, and less sterically available sites for water. Interestingly, the enhanced crystallinity of the films was associated with a decrease in intermolecular water (Figure 1f). Considering that the films were initially at equilibrium with the environmental humidity, this result suggests a role for the secondary reorientation of chitin during molting in cuticular water removal, a process generally attributed to sclerotization.[15]

From a mechanical perspective, the randomized alignment of the crystal domains in the unaligned films resulted in tensile properties independent of the pulling direction. The films were also characterized by prevalent plastic energy absorption under stress and ultimate tensile stress in the range of commodity plastics (45Mpa; **Figure 2**a,b). On the other hand, uniaxially reoriented films had similar toughness but more than twice the strength of unstretched films, demonstrating a characteristic combination of toughness and strength of structural biomaterials that nonhierarchical materials struggle to achieve.[16] Furthermore, the reconfigured material absorbed most of the energy elastically, showing mechanical enhancement approaches similar to those used by arthropods in their outstanding protective shells, impact-resistant appendages, and lightweight and stiff wings.

We have demonstrated that the secondary reorientation of chitin in arthropods during molting and the associated change in intermolecular water can be artificially reproduced to enhance the mechanical properties of chitinous materials. In structural biomaterials, the interplay between forces, molecular organization, and water exchange is based on bidirectional relationships between them, enabling the passive generation of movement and forces in response to environmental changes in mature cuticles. This phenomenon is also very apparent in plants where, without a nervous system, the ability to embed a programmable task in the material becomes even more critical.[17] A well-known example is the use of cellulose fibers' orientation in pine cones for the autonomous opening and release of the cone's seeds when the environmental conditions are appropriate for germination.[18,19] In insects, the interplay between fiber alignment, mechanical properties, and passive force generation is conveyed in the chitinous cuticle of *Rhodnius Prolixus*, which uses pH changes and intermolecular water to expand and contract its abdomen in response to food availability.[20]

We tested the ability of chitinous polymers to generate force through water exchange by clamping chitinous films in a tensile tester and subjecting them to dehydration under hot air (Figure 2c). The unstretched chitosan films of 130.5 μm thickness and 2 cm width were able to pull objects of >4.5 Kg (i.e., 45 N and 36 MPa) when drier than their equilibrium condition with respect to environmental humidity (RH = 80%; Figure 2d,e). To our knowledge, this is the largest pulling force generated by a humidity-responsive material, and it is several orders of magnitude higher than other materials specifically designed and synthesized for this purpose, such as VONW films (6.5 KPa)[21] and PILTf2N membranes (25 KPa).[22] Notably, this achievement was reported for an unmodified biomaterial of known biocompatibility, highlighting the potential use of passive actuation in medical applications.[23] However, hygroscopic actuation was negatively affected by enhanced crystallinity and molecular orientation, suggesting that the space occupied by some water expelled during stress-induced crystallization was irreversibly lost. This reduction in the hygroscopic pulling force was particularly significant in the direction of uniaxial stress, suggesting that, similar to the cellulose orientation in plants, the hygroscopic forces in highly oriented chitinous biopolymers dominate in the direction perpendicular to the alignment.[19] Therefore, an optimal design of chitinous composites (e.g., the arthropod cuticle or structural passive actuators) with enhanced mechanical strength and water-driven actuation is one with highly oriented fibers along the direction perpendicular to the actuation.[24]

The films' force output and contraction speeds make them appropriate for large-scale applications of passive actuation, including smart architectural constructions, such as canopies that automatically deploy and contract in response to rain.[25] A unique potential of the hygroscopic films used in this study arises from their unmodified chitosan composition, a material native to every ecosystem and with a demonstrated lack of human immune response, which enables seamless integration of passive actuation in biological systems at human to ecological scales. We tested the suitability of the material for the actuation of a simplified bionic limb by assembling chitinous films in a mechanical hand. The fingers were made of three rigid segments actuated by a single pulling mechanism (**Figure 3**a). Each pair of fingers (the thumb was not actuated in this setup) was connected to a 20 cm long, 2 cm wide, and 130.5 μm thick chitinous film. Each film displaces ≈1 cm when it is drier than the equilibrium condition with respect to Singapore's tropical environment (80% RH), which is sufficient to cover the range of movement between a closed and an open hand (Figure 3b and Video S1, Supporting Information). With a force of 90N per film, the total gripping force of the hand was equivalent to 18 Kg, more than half the average grip strength of adults (i.e., 30.6 Kg). However, despite the strong forces produced by the biocompatible and relatively thin chitinous films, their integration with biological systems is limited by a hygroscopic mechanism based on evaporation. For


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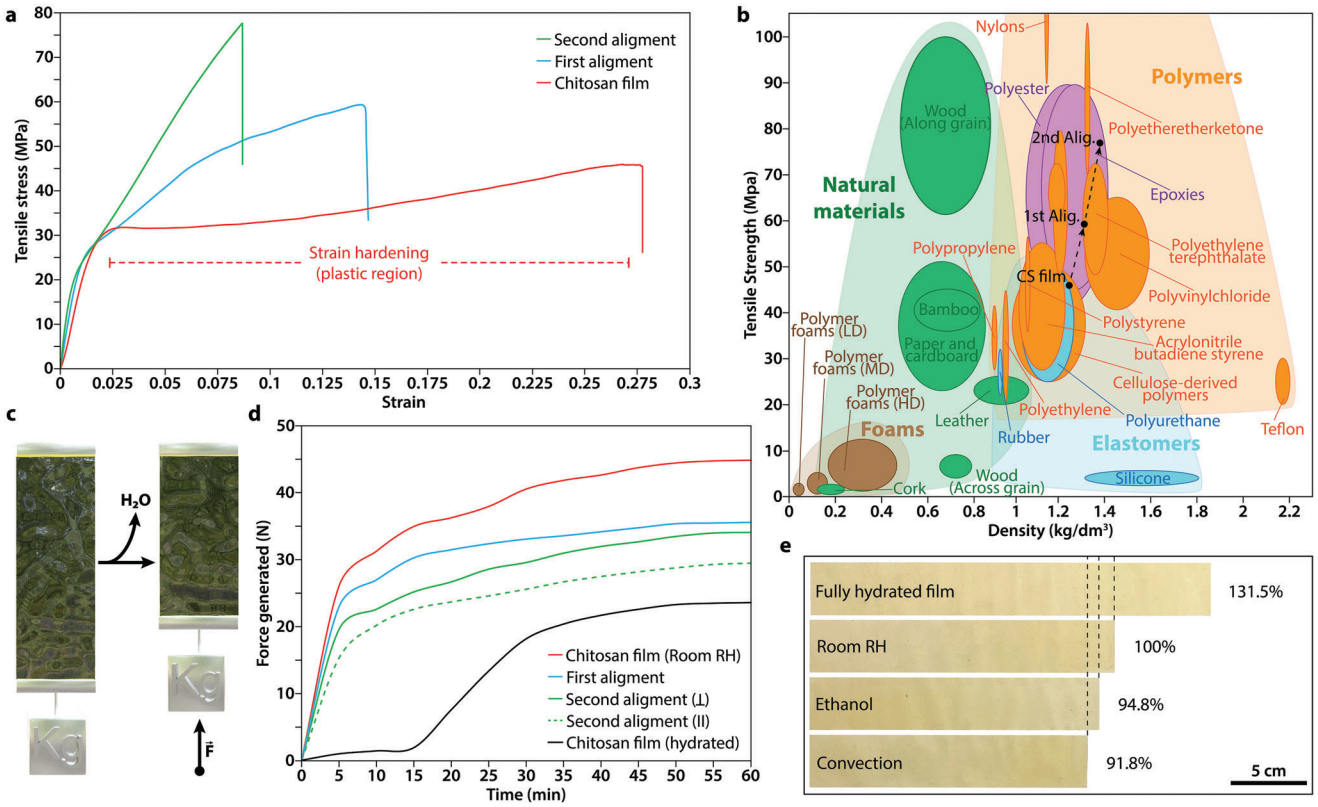



**Figure 2.** Mechanical effects of secondary realignment and humidity changes. a) Mechanical characterization of the chitinous films after stretching. Because of the uniaxial reorganization of chitinous molecules, the films demonstrated a characteristic combination of the strength and toughness of natural bio composites. After stretching, the original material, which was tough but soft and similar to a newly molted cuticle, transformed into a stiff material that resembled the mature cuticle, and became suitable for protecting the animal from external impact. b) After consecutive realignments, the tensile strength of the chitinous films changed from a value similar to the tensile strength of commodity plastics (e.g., PS, PET, and PE) to that of polymers used for specialized engineering applications (e.g., PEEK). c) Diagrammatic representation of the application of hygroscopic actuation in chitosan films. The films' ability to relax and contract due to passive water absorption and release enabled the generation of forces. d) Forces produced by chitinous films that are 125 µm thick and 1 cm wide while drying. After immersion, the water-saturated films (illustrated by the black line) generated relatively low forces until a sufficient amount of water was released. In contrast, films at equilibrium with atmospheric humidity demonstrated strong actuation in response to dehydration. Despite the mechanical enhancements, the improved molecular organization in the stretched films limited the amount of intermolecular water accumulable, which resulted in weaker but still substantial actuation forces. The reduction in force generation was more significant along the direction of the polymer alignment (indicated by the dashed green line) compared to the direction perpendicular to it (indicated by the solid green line). e) Image of the chitinous films in various hydration states. Water-saturated films at equilibrium with ambient humidity expanded one-third of their length. Films dried using a chemical (ethanol) or physical (hot air) approach showed significant differences in their actuation potential.

their effective integration with a host organism, such as artificial muscles, biomedical implants, and metabolic energy harvesters, the films must produce force utilizing native water transport mechanisms based on biochemical processes.[26]

We tested the response of hygroscopic actuation to common biological drying/wetting agents using ethanol as a dehydrating agent (Figure 2e and Figure 3c). In samples at equilibrium with the environment, we observed the ethanol-driven actuation to be 1.7 times faster than the actuation triggered by forcing water evaporation with hot air, demonstrating the effectiveness of the process and the resonance of the chitinous hygroscopic actuation with other biological principles and strategies. Chemical actuation is, however, not without drawbacks. Passive actuation by evaporation is a continuous process in which free water is exchanged between the material and an absorbing atmosphere of constant properties (i.e., a thermodynamic sink). In chemically actuated films, the water expelled into the environment produces a dilution of the dehydrating agent and, therefore, a decline in its ability to remove water further. This decreasing efficiency was reflected in the constant decrease in the actuation speed of the chemically driven films with respect to those dried using hot air, which ultimately resulted in significantly different displacements. These observations, which result from a relatively pliable environment, are unlikely in biological systems, in which the environment is continuously renewed and chemical agents are locally secreted. Similarly, in artificial applications, an on-demand environmental change (e.g., release of a dehydrating agent or water) is the most likely implementation of a chemically driven actuation, since this approach also overcomes the decrease in effectiveness due to water saturation of the environment.

One of the advantages of using native biological tools instead of electrical devices to integrate actuation into biological systems is the avoidance of electrical energy inputs. However, the completion of a programmed task without electricity is not possible


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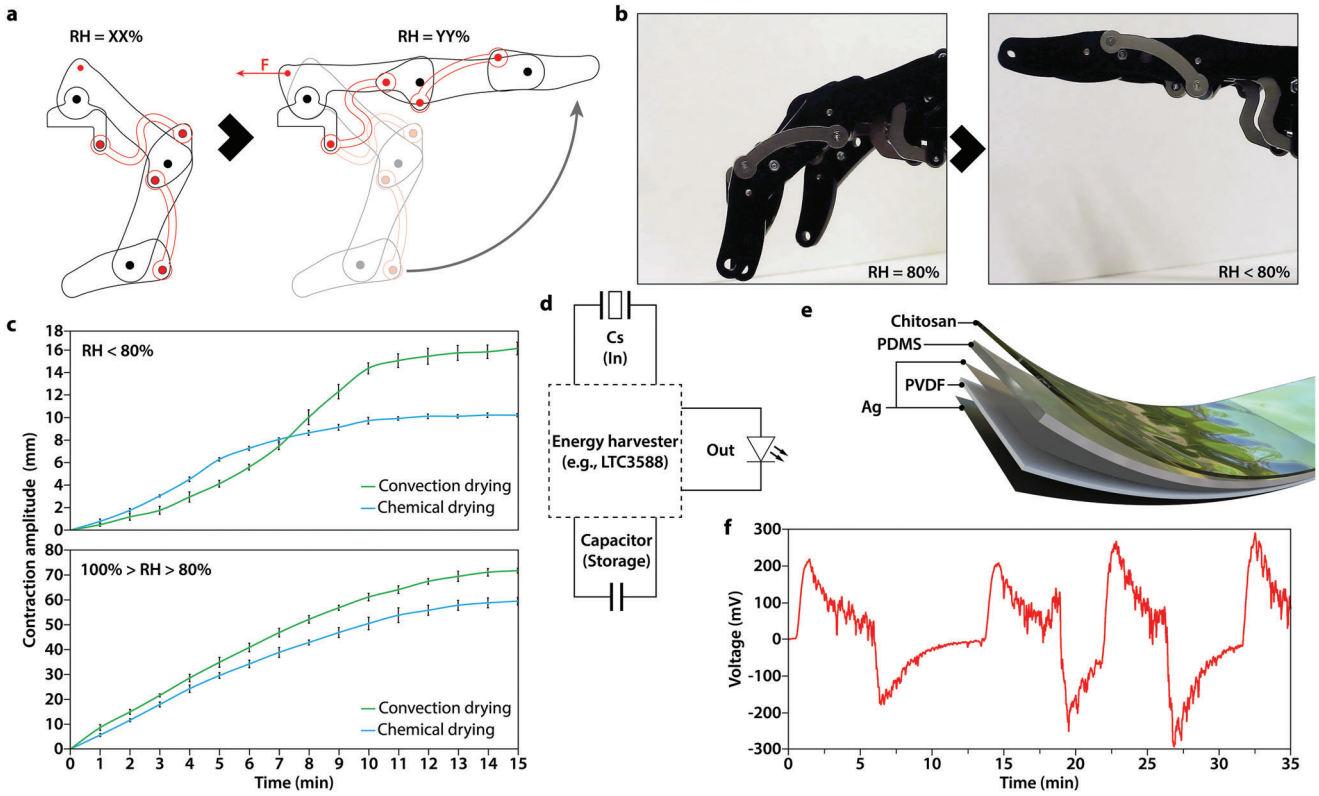



**Figure 3.** Application of chitinous hygroscopic actuation for artificial muscles and energy harvesters. a) Diagrammatic representation of the articulated finger actuated by a uniaxial force. Each finger comprised three segments and rotational joints. The whole system can be actuated using a single pulling force (indicated as F in the diagram). In our case, this was exerted by the chitinous films in response to changes in humidity. b) Pictures of the four fingers at equilibrium with atmospheric humidity (left) and after drying (right). For an in-depth analysis of the hand actuation, please refer to Video S1 (Supporting Information). c) Differences between chemically (ethanol) and physically (hot air) actuated chitinous films. Films at equilibrium with atmospheric humidity (top graph) showed faster actuation when immersed in ethanol. This advantage was reduced as more water was expelled; ultimately, more significant actuation was achieved with hot air. This suggests that chemical actuation is more suitable for rapid but shorter moves, while air drying results in slower movements but higher amplitudes. The limited potential of ethanol to remove large amounts of water was more evident in water-saturated films (bottom graph). d) Diagram of a model circuit for hygroscopic energy harvesting using a combination of passive actuation with chitinous films, a piezoelectric generator, a buck converter, and an optional storage unit. e) Diagram of multilayered chitinous films for energy production. Chitinous films were produced on a functionalized PDMS surface attached to a custom-made piezoelectric film. Changes in atmospheric humidity resulted in the expansion/contraction of the films, bending of the structure, and generation of an electrical current. f) Current generated by the chitinous hydroelectric generator after four drying/relaxing cycles. For a detailed video of the film and the electricity generation process, please refer to Video S2 (Supporting Information).

when the task requires sensing or actuation beyond biological specialization. In these cases, the use of an electrically powered device is necessary. We explored bridging the electrical and biological realms by producing electricity with chitinous films (Figure 3d and Video S2, Supporting Information). The films' horizontal movement was limited by flexible support provided by an elastomeric polymer (dimethylpolysiloxane, PDMS), converting their longitudinal actuation into a bending actuation. The bending movement was then converted into an electric output by attaching a thin film piezoelectric component composed of a 28 µm thick polyvinylidene fluoride (PVDF) membrane with silver metallization on each side (Figure 3e). Other metallization's (e.g., NiCu) would allow more efficient energy conversion. In this study, we used silver paint because of its flexibility and ability to easily cover large surfaces without any specialized equipment (e.g., a metal sputtering machine). The hygroelectric generator was sequentially dried and equilibrated with atmospheric humidity to simulate the effects of a changing environment. This resulted in the production of electric currents of hundreds of mV for several minutes during each cycle (Figure 3f). This voltage is well within the range of what is used by modern energy harvesters to power small electronics.[27,28] The proposed hygroscopic generator does not replace kinetic energy harvesters but presents an alternative to utilize, on its own or in combination with other types of energy harvesters, environmental changes associated with natural systems. An example application would be an energy harvest from moisture changes during breathing or ventilation,[29] a task that would otherwise require obstructing normal airflow with a kinetic energy harvester.

## 3. Conclusion

We demonstrated stress stiffening and secondary realignment of chitinous films in response to external forces and the impact of


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these processes on their crystallinity, physical properties, and water content. The relationship between free water and the molecular arrangement was used to exploit the hygroscopic abilities of thin chitinous films for passive actuation. This study demonstrated that 130.5 μm thick and 2 cm wide chitinous films generated forces greater than 45N in response to environmental humidity changes. The same response of chitinous films was also reproduced using chemically driven dehydration with ethanol, a process similar to metabolically induced movement in organisms. The films' potential was demonstrated using example applications: to power a mechanical hand's grab-release movement and to produce electricity from humidity changes.

These results highlight the engineering potential of combining unmodified structural biomolecules, which are otherwise considered waste, with their native functionalities. This novel approach demonstrated the engineering application of materials and processes involved in the molting of arthropod cuticles and explored new technologies and solutions that can be seamlessly integrated with biological systems from a cellular to an ecological scale.[30]

## Supporting Information

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

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## Conflict of Interest

The authors declare no conflict of interest.

## Author Contributions

J.G.F. conceived the use of the native hygroscopic actuation of chitinous polymers in artificial systems. K.J.T performed the initial experiments using architectural constructs. B.R. and J.G.F. designed the experiments and analyzed the data. B.R. performed the experiments and collected the data. J.G.F wrote the first draft of the article. All authors contributed to writing the manuscript.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

## Keywords

bioinspired manufacturing, chitin, hygroscopic materials, passive actuation

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