Magnetostrictive and Electroconductive Stress-Sensitive Functional Spider Silk

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Electronics and soft robotics demand the development of a new generation of hybrid materials featuring novel properties. Among these, remarkable mechanical properties are required to sustain mechanical stresses, and electrical and magnetic properties are essential to design the devices' interface. In this work, a hybrid material is presented, consisting of a spider silk thread, providing mechanical robustness, coated with a layer of a magnetostrictive FeCo alloy, which ensures both electrical conductivity and stress-sensitive magnetic properties. The durability and the homogeneity of the composite are validated, as well as its ability to respond to magnetic and mechanical stimuli. Despite the coating, the soft nature of the silk and its mechanical performances are preserved. The magnetic study reveals that the magnetic behavior of the film is strongly affected by the silk thread-FeCo layer interaction, especially under mechanical stresses. Indeed, when the composite is subjected to tensile strain, the magnetic signal changes accordingly, indicating that the layer-silk interaction is maintained and can be exploited to reveal the tensional state of the sample even under severe cycles. Therefore, the presented hybrid material is a flexible fiber with properties that are suitable for magneto-electronics applications, e.g., magnetic actuators as well as strain/stress sensors.

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1. Introduction

The development of flexible materials with magnetic and electronic properties has raised in these decades the interest of scientists due to their technological potential.^[1,2] The aim of these materials is to provide integrated solutions that offer both electrical and magnetic properties combined with stretchability, compressibility, twistability, bendability, and in general deformability.

Common electronics and magnetic materials, such as silicon or ferromagnetic alloys, are rigid and fragile. On the contrary, many biological materials are soft, elastic, and offer inspiration to design structural materials with desired properties.^[3,4] For example, artificial skin that resembles the natural counterpart may be used in soft robotics, provided its mechanical similarity with respect to the natural skin.^[5,6] Artificial skin also provides a roadway toward wearable sensing devices, which enables a natural interaction

between the body and the device itself, allowing people to have a personalized healthcare.^[7] Moreover, these devices are stretchable and possibly fatigue free while performing their monitoring functions that integrate physical and chemical features on the same wearable platform.^[8] Thus, the aimed flexible electronics devices must sustain repeated bending and stretching as well as have the possibility to perform multiple functions. Furthermore, to reduce the impact of the electronics contacts, the components of the electronic devices must be micrometric in size (wires of $\approx 2-10 \ \mu m$ in diameter)^[9] and lightweight.^[10] In this context, magnetic actuation fibers (e.g., amorphous magnetic microwires^[11]) play a crucial role in soft robotics, since they combine the high tensile strength with the high compliance and desired functionality.^[12] Magnetic actuation fibers can be produced in several ways:^[12] coating fibers with water based solutions,^[13] electrospinning,^[14] and 3D printing of the magnetic microparticles-polymers composites.^[12]

To expand such frontiers, silk represents a good basic material for such soft components, since its properties align with the ones of many soft tissues, and thus it allows scientists to achieve a smaller mismatch in mechanical properties between electronics component and the working environment.^[1,9,15] In terms of mechanical properties, silk can be used in a composite to provide compliance and stretchability as well as strength to weak materials.^[16] However, having a poor conductivity, silks need to

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be hybridized with materials that can convey such property. In this context, silkworm silk has been used to produce electrical devices, such as electronic skin for medical applications.^[17] Unfortunately, despite the acceptable conductivity, many silkworm silk based devices present poor mechanical properties,^[18,19] which can be overcome by using spider silk instead. In fact, although silks are produced by several arthropods, the spider ones have been studied since a long time^[20,21] because of their superior mechanical and biological properties with respect to the silkworms.^[22–26]

Therefore, spider silk was hybridized to produce a magnetic composite by using a water dispersion of magnetic particles.^[27] However, due to the exposure to water that irreversibly plasticizes spider silks,^[28,29] the produced material presented reduced mechanical properties.^[26,30] Unfortunately, no magnetic as well as electric characterization was available.

To hybridize spider silks with metals, the exposure of the fibers to vapors doped with heavy metals seemed to improve the mechanical properties.^[31] However, also in this case no electronic and magnetic characterizations were performed. In this regard, the deposition of evaporated gold on spider silk provides electrical conductivity, which resists if the composite works with deformations below the yielding point.^[32]

Spider silk may be also hybridized with nanomaterials, such as graphene^[33] or carbon nanotubes^[34,35]. Spider silk bundles have been combined with carbon nanotubes by means of a water dispersion.^[34] Despite the decrease in strength due to water, the silk presented still acceptable mechanical properties, as well as a good conductivity that was preserved also after strain cycles. Another example is represented by the electro-tendon presented in Pan et al.^[35] Spider silk may also be used as a binding agent for Si-based electrodes, which seem to provide superior electrochemical performances.^[36] Singh et al. produced a composite by mixing dissolved silk with Fe₃O₄, but no magnetic characterization was performed.^[37] Thus, despite a certain number of hybrid spider-silk magnetic materials have been produced, there is scarce knowledge about their magnetic properties, and how these are in synergy with the mechanical ones.

In this work, we present a simple method to produce a hybrid material composed of a spider silk thread, with micrometric diameter, coated with a ferromagnetic magnetostrictive layer (Fe₅₀Co₅₀ alloy) (Figure 1a-d). The combination of these two elements results in a wire-like ferromagnetic metallic system, which retains its electrical conductivity under strain, highly flexible and extensible-so that it can be modified in shape as well as modeled to act as a component according to specific applications (Figure 1f)-and displaying good mechanical performances. Moreover, the hybrid system features magneto-mechanical coupling, i.e., its magnetic response can be varied by applying a mechanical strain, and it is able to actuate stresses that outperform many magnetic actuators. Therefore, multifunctional hybrid systems of this kind have the potential for being exploited as basic components in electronics and soft robotics applications, such as sensing or actuation.

2. Results

In this study, we used the dragline silk threads (STs) (Figure 1a) produced by *Cupiennius salei* (Keyserling 1877)^[38]

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and composed by at least two silk fibers (Figure 1b). The STs were collected and then prepared for further characterization following the procedure reported by Blackledge et al.,^[38] namely each ST was cut into pieces of the desired length and then fixed on a cardboard frame with a double-sided tape (Figure 1c). To obtain the magnetic silk threads (MSTs), the STs were covered with a 100 nm thick magnetic Fe₅₀Co₅₀ (FeCo) layer. The layer was deposited in Ar atmosphere (Ar pressure \approx 0.1 Pa) using a high-vacuum dc magnetron sputtering apparatus (base pressure \approx 10⁻⁵ Pa; Figure 1d,e). Due to that, as a control, vacuum silk threads (VSTs) were also prepared by exposing the STs to a high vacuum stage comparable to that used for the MSTs preparation.

2.1. Scanning Electron Microscopy

Figure 2 shows representative scanning electron microscopy (SEM) images recorded on an MST sample after performing the tensile tests, by collecting both secondary (Figure 2a,b) and backscattered (Figure 2c,d) electrons. The morphology of the MST was not significantly affected by the coating procedure, and was similar to that of ST (Figure 1b). The quality of the coating was also investigated with SEM backscattered electrons detector. In particular, the compositional contrast (Figure 2c,d) appeared uniform and the Energy dispersive X-ray spectroscopy (EDXS) analysis (Figure S1, Supporting Information) confirmed the presence of the FeCo layer. These results indicate that the FeCo coating of each of the silk fibers composing the thread was uniform.

The diameter of the threads was measured by means of optical microscopy. The average diameter value is $9 \pm 5 \,\mu\text{m}$ for both MSTs and VSTs, while for the STs the measured value is $11 \pm 5 \,\mu\text{m}$. The typical size of a single silk fiber, as obtained by SEM measurements, is $\approx 1 \,\mu\text{m}$.

2.2. Electrical Conductivity

The results of the electrical conductivity measurements are presented in Figure 3. Figure 3a shows a representative potential difference-current curve (i.e., ΔV versus I), measured on 5 mm long MSTs. The trend is linear, and the same is found for negative current values, which is consistent with an ohmic type conduction. The obtained electrical resistance value, i.e., the slope of the ΔV versus I curve, was $R_{MST} = 11.13 \pm 0.03 \text{ k}\Omega$. Figure 3b reports the ΔV versus eng. strain ε dependence for the MST sample when $I = 7 \mu A$. Two different regimes are observed: at first, ΔV increases linearly, tripling its value, on increasing the applied strain up to ≈0.02; at higher strain, ΔV is nearly constant and reaches a plateau value till the fracture of the magnetic layer, and thus loss of continuity, at ε = 0.08. In these experiments, a selected maximum strain was cyclically applied in order to verify that the conductivity did not drop to zero, i.e., the coating was not stripped (if the strain was lower than 0.08). More details on the effect of the cyclic loadings on the electrical conductivity of the MSTs are reported in Supporting Information Section S2.

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2.3. Mechanical Characterization

10 µm

a)

f)

b)

Tensile tests were performed on both STs and MSTs. The transformation of STs in MSTs involved two steps, namely the permanence in a high vacuum chamber and the deposition of the FeCo coating (section "Spider Silk Coating"). Therefore, to disentangle the effect of the two steps on the mechanical properties and to pinpoint the contribution of the metallic layer, we also prepared an additional set of samples, VSTs. VSTs were obtained by exposing the STs to a high vacuum stage comparable to that used for the preparation of the MSTs, i.e., they were kept at 10^{-5} Pa for ≈ 50 min. Table 1 and Figure 4 display the results of the mechanical characterization (the *p*-values of the pairwise comparisons are listed in Tables S1-S4, Supporting Information). The mechanical properties and the diameters of the raw material, ST, are comparable to those reported in the literature and display the same inherent variability.^[22,23,26,39-41] The permanence in high vacuum seemed to plasticize the threads by improving their deformability (the strain at break of the VSTs was significantly

the highest) whereas the presence of the metallic coating seemed to slightly reduce it. Moreover, the high vacuum stage also seemed to have a marked effect on the mechanical properties of the fibers (strength, especially), as the STs presented the highest strength in comparison to the MSTs and VSTs. Nevertheless, the Young's modulus of the MSTs was the same as the native ones and only the VSTs were significantly softened. The highest toughness was the one of the STs, probably due to the strength reduction observed for both MSTs and VSTs. Lastly, we found that, for the three groups of samples, in particular the VST and the MST ones, the strength and the Young's modulus are negatively correlated with the diameter (Figure S3, Supporting Information), as is usually observed in silk fibers.^[42]

The maximum likelihood method^[22,43] was used to calculate Weibull parameters for the three types of tested samples (scale and shape; Table 1). The strength Weibull distributions of the samples are depicted in Figure 4f, and the narrower one belonged to the coated samples, which indicates a more homogeneous behavior in terms of fracture.^[22]





Figure 2. SEM images of a MST sample, recorded after tensile tests, and obtained collecting secondary electrons (a,b) or backscattered electrons (c,d). The scale bar corresponds to $2 \,\mu$ m.

2.4. Magnetic Properties

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In addition to the MSTs, we also prepared a reference magnetic sample by sputtering a 100 nm thick FeCo film on a planar naturally oxidized silicon substrate, under the same

experimental conditions adopted for coating the STs. This reference film was labeled as ${\rm FeCo}_{\rm ref}$

Figure 5a shows the magnetic hysteresis loops measured by superconducting quantum interference device (SQUID) magnetometry on FeCo_{ref}, at room temperature, by applying the



Figure 3. a) $\Delta V-I$ curve of the MST measured in the lab; the electrical resistance value obtained from the slope of the linear dependence is $R_{MST} \approx 11 \text{ k}\Omega$. b) Graph of the potential difference measured on the MST versus the eng. strain ε applied to it.

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Type of silk	Diameter [µm]	Strain at break [mm mm ⁻¹]	Strength [MPa]	Young's modulus [GPa]	Toughness modulus [MJ m ⁻³]	Scale Parameter [MPa]	Shape Parameter
ST	11 ± 5	0.28 ± 0.10	365 ± 290	5.2 ± 4.8	61±46	382	1.41
MST	9 ± 5	$\textbf{0.23} \pm \textbf{0.18}$	102 ± 85	4.9 ± 3.7	22 ± 24	111	1.33
VST	9 ± 5	$\textbf{0.63} \pm \textbf{0.22}$	93 ± 88	2.0 ± 1.9	29 ± 19	85	1.03

 Table 1. Mechanical properties and Weibull parameters of the tested samples.

magnetic field *H* along two arbitrary orthogonal directions in the plane of the film, labeled as $\theta = 0^{\circ}$ and $\theta = 90^{\circ}$. The obtained loops are squared, which indicates that the magnetization lies in the plane of the film under the prevailing action of the shape anisotropy. However, the shape of the loops does not depend on the applied field orientation, i.e., the sample is magnetically isotropic in the plane. The saturation magnetization of the film is $M_S = 1.75 \times 10^6$ A m⁻¹, the coercivity H_C is ~11.5 kA m⁻¹ and the irreversibility field H_{IRR} , i.e., the field value at which the two branches of the loop join, is ~12.7 kA m⁻¹ (Table 2). The M_S value is slightly smaller than that of bulk FeCo (i.e., 1.91×10^6 A m⁻¹),^[44] which can be due to a partial oxidation of the FeCo layer and/or to a mass density reduction often observed in sputtered thin films.^[45] Differently, both H_C and H_{IRR} are very high with respect to the bulk ones that, for the ordered alloy, are of the order of 1 Oe.^[44] The analysis performed by magneto-optic Kerr effect (MOKE) magnetometry on FeCo_{ref} confirms the H_C and H_{IRR} values obtained by SQUID.

Figure 5b shows the hysteresis loop measured by SQUID on the MSTs with *H* applied parallel to their long axis. To increase the intensity of the magnetic signal, three 5 mm long MSTs were measured at the same time. The measured magnetic moment at saturation is $\mu_{sat} = 7.74 \times 10^{-8}$ A m²; H_C is ≈ 23.9 kA m⁻¹ and $H_{IRR} \approx 43.8$ kA m⁻¹, higher than those measured on FeCo_{ref}. If we approximate each MST by a ferromagnetic microtube with length of 5 mm, diameter of 9 μ m (Section 2.1), thickness of 100 nm, with a M_S equal to the FeCo_{ref} one, the expected magnetic moment for three MSTs is 7.5 $\times 10^{-8}$ A m². This result



Figure 4. a) Representative engineering stress-engineering strain curves of the tested samples. b) Strain at break, c) Young's modulus, d) strength, and e) toughness modulus of the tested samples. f) Weibull distribution of strength of the analyzed samples. Stars indicate that the difference is significant (*p*-value < 0.05).

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Figure 5. a) SQUID magnetic hysteresis loops measured at room temperature on the reference 100 nm thick FeCo film (FeCo_{ref}) with the external field applied parallel to the plane of the film, along two arbitrary orthogonal directions, labeled as $\theta = 0^{\circ}$ and $\theta = 90^{\circ}$. b) SQUID magnetic hysteresis loop measured at room temperature on three MSTs with the applied field parallel to the MSTs direction. c) Comparison between the MOKE signal recorded on an unstrained MST (full black symbols) and the MOKE signal collected on an MST subjected to an engineering strain $\varepsilon = 0.025$ (full red symbols). In both cases, the direction of the applied magnetic field is parallel to the MST and the measurements were performed at room temperature.

is close to the measured one, thus supporting the fact that the MSTs display a bundle structure and suggesting that the FeCo coating maintains its $M_{\rm S}$ value.

We also performed a magnetic characterization using MOKE magnetometry. The loops measured on a single MST (with *H* parallel to its long axis) with no strain (i.e., $\varepsilon = 0$) and under a tensile strain $\varepsilon = 0.025$ are shown in Figure 5c. We used a small strain value in order to reduce cracks formation.^[46–48] In the unstrained condition, the magnetization reversal process is less sharp than that observed in FeCo_{ref} (Figure 5a) and even less in the strained state. The values of H_C and H_{IRR} increase considerably when passing from the unstrained to the

strained state. MOKE measurements were also performed after subjecting MSTs to cyclic tensile loadings, to check if this procedure affected the magnetic properties. More details about this point are reported in Supporting Information Section S2.

2.5. AFM and MFM Analysis

A combined atomic force (AFM) and magnetic force (MFM) microscopy analysis of the MSTs was performed in order to access both their morphology and their magnetic configuration. **Figure 6**a confirms the bundle structure of the MST.

Table 2.	Coercivity H _C and irr	eversibility field H _{IRR} v	alues for the different	: samples. H _C and H _I	IRR for the bulk case were	obtained from Ref. [44]
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Samples	Method	H_{C} [kA m ⁻¹] ± 2%	H_{IRR} [kA m ⁻¹] ± 2%
FeCo bulk	Ref. [44]	≈0.1	≈0.1
FeCo _{ref}	SQUID/MOKE	11.5	12.7
MST	SQUID	23.9	43.8
	MOKE	25.5	46.2
MST, <i>ε</i> = 0.025	MOKE	32.6	75.6



Figure 6. a) AFM and b) MFM maps recorded on a region of a MST where the presence of the bundle structure can be clearly observed. In (a), some sub-micrometric particles, probably dust, can be observed. In (b), the white dashed lines represent the lateral sides of the fibers; each red (violet) arrow points to the side close to which the regions characterized by a red (violet) MFM contrast are located. Comparison between the 3D magnetic reconstructions, resulting from the combination of the 3D morphology, as obtained from AFM profiles, and of the magnetic contrast, as obtained from MFM profiles, of the unstrained MST (c), and of the same MST whilst that is strained (ε = 0.025) (d). Regarding the magnetic phase contrast, panels (c) and (d) share the color scale reported in panel (b).

The FeCo layer, which seems to cover the fibers in a rather uniform fashion, presents a smooth surface, with a mean roughness of \approx 3 nm (see also Figure S4, Supporting Information). In Figure 6b, the MFM profile of the same sample region is displayed. Areas showing a pronounced magnetic contrast are aligned near the grooves between adjacent fibers. In more detail, areas displaying a negative (red) contrast are found on one side of the fibers and those showing a positive (violet) contrast are located on the opposite side. Differently, in the other portions of the fibers (i.e., making reference to the height scale, at the top of each fiber) the contrast appears to be smoother.

We also performed the AFM-MFM analysis in a strained condition equal to that used for MOKE measurements (i.e., $\varepsilon = 0.025$). The effect of the strain can be well appreciated by comparing the 3D maps displayed in Figure 6c,d. In these maps the MFM signal has been superimposed to the morphology of the MST, reconstructed using the AFM map, in order to better highlight the position where a specific MFM signal is detected. Figure 6c refers to the $\varepsilon = 0$ case, while Figure 6d to the $\varepsilon = 0.025$ one. Overall, in Figure 6d, there is a strong reduction of the magnetic contrast at the sides of the fibers with respect to Figure 6c.

2.6. Magnetic Actuation

The magnetic actuation was evaluated by clamping the MST in the nanotensile machine at fixed distance (the MST were in tension at 0.5%) and by measuring the load while the commercial magnets were approached to the sample (Figure 7a). The magnetic configuration of the commercial magnets is presented in Figure 7b, while the dependence of the intensity of the magnetic induction *B* as a function of the distance from the magnets, measured along the magnets to MST direction (represented by the green arrow in Figure 7b), is displayed in Figure 7c (Video S1, Supporting Information). The B intensity changes rapidly as the distance is varied, thus revealing the non-uniformity of the B configuration. This conclusion is also supported by the *B* intensity map displayed in Figure S5b (Supporting Information). The load increases with the approaching of the magnets (Figure 7b) up to a value of 0.12 mN that, considering that the diameter of the used thread was $\approx 5 \ \mu m$, corresponds to a maximal stress of $\approx 10 \ MPa$. That value was measured when the magnet was almost in contact with the MST (distance ≈ 0 cm), and it was cyclically consistent upon different approaches (Figure S6, Supporting Information).



Figure 7. a) Scheme of the experimental setup used to access the effect of the actuation induced by the magnets on MSTs. Starting from a distance of \approx 4 cm, the commercial magnets were approached till almost the contact with MST. b) Representation of the north (N/red) and south (S/blue) poles configuration of a single commercial magnet (upper part), and of the group of magnets used for the experiment (lower part). c) Dependence of the magnetic induction intensity, measured along the path represented by the green arrow in panel (b), as a function of the distance from the front side of the group of magnets. The dotted line is a guide to the eye. d) Nanotensile machine load on the MST as a function of the distance of the commercial magnets from the MST.

3. Discussion

In this work, spider silk threads have been collected and used as a basic material in view of the production of micromagnetic multifunctional devices. This has been done by coating the samples with a 100 nm thick magnetostrictive FeCo layer.

The FeCo coated threads retained their original shape, which is essentially cylindrical, albeit with a bundle morphology (Figure 2). Only a small reduction in diameter was observed, in agreement with literature's results (decrease of $\approx 10\%$) and due to the dehydration of the sample during vacuum exposure.^[49,50] The stability over time and uniformity of the FeCo coating were assessed by EDXS and SEM analyses. The coating was seen to cover the fibers also after the mechanical tests, i.e., after breaking the MSTs. These results support the good silk-FeCo coating adhesion.

Electrical resistivity values, measured both on strained and unstrained MSTs, are of the order of $10^4 \Omega$, suitable for many electronics applications.^[9] For comparison, we estimated the resistance, R_{th} , of a MST modelled as a cylinder with length 5 mm, diameter 9 μ m (see Section 2.1), and uniformly covered with a 100 nm thick FeCo layer. Since the resistivity measured on the FeCo_{ref} film was $30 \times 10^{-8} \Omega$ m, from the second Ohm's law we obtained $R_{th} = 0.5 \ k\Omega$, which is lower than R_{MST} . Due to shadowing effects related to the sputtering deposition method,^[51] the thickness of the FeCo layer in the interstices between adjacent fibers may be lower than the nominal value. As a consequence, the value of R_{th} could be underestimated. Moreover, the high R_{MST} value suggests that the FeCo coating, grown on a flexible substrate, most likely has a higher defect density and therefore a higher resistivity compared to the FeCo_{ref} film, which was deposited on a rigid planar substrate.^[52] On the other hand, the presence of defects does not imply the existence of a significant number of discontinuities in the FeCo coating. In fact, in that case, both a much higher resistance value and a non-linear ΔV versus *I* curve would be measured.^[53,54] Hence, the R_{MST} value is in favor of a metallic covering providing a good degree of electrical continuity.

For comparison, a resistance as high as $\approx 10^5 \Omega$ was measured on ≈ 20 mm long spider silk threads coated with a 100 nm thick gold layer.^[32] Electronic devices based on spider silk were also designed by hybridizing it with graphene (with a resistivity circa ten times higher than that of MST^[33]) and carbon nanotubes.^[34,35] In these systems, resistance values similar to those measured in our MSTs were obtained when the temperature was several degrees below 0 °C. Moreover, the resistance of carbon nanotubes-based devices was seen to increase tremendously with the strain. In particular, at 10% of strain the resistance was over 1 M Ω , which is almost 90 times the value

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found for the MSTs at a similar level of strain (\approx 33 k Ω at 8% of strain, Figure 3). The initial increase in resistivity that was here observed is in agreement with other authors when applying a tensile strain to samples produced by growing a metallic film on a planar elastic substrate. This effect was ascribed to the formation of cracks in the metallic layer,^[47,55] and the relative variation of resistance was of some orders of magnitude.^[47] In our case, cracks may develop starting from the interstitial regions between adjacent fibers, where the thickness of the FeCo film is smaller, with respect to the other parts of the thread, and so the stress on it is higher.^[56] In this way, resistance increases but electrical continuity is preserved. It is expected that, as the strain increases, the cracks density reaches a constant value,^[47,48,57] and therefore the resistance does not change further, as indeed observed in our case. Eventually, when the strain is ≈ 0.08 , cracks may appear orthogonally to the fibers, [47,57,58] and/or the thread may fray, so the electrical continuity is lost. This value of the upper strain limit for electrical conduction is higher with respect to those reported in literature related to similar systems.^[32,33] In summary, these data highlight the potential of the MSTs, as useful resistance values are obtained at room temperature and no variation of the order of magnitude is produced under strained conditions.

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As for the mechanical performance, with respect to the STs, the MSTs exhibited comparable values of strain at break and Young's modulus, and smaller values of toughness modulus and strength (Figure 4). The same Young's modulus values could be explained by the presence of the stiff magnetic coating, which could have compensated the plasticization induced by the vacuum. The observed modifications may be ascribed to different factors: the presence of the metallic coating, the exposition of the silk fibers to a high vacuum environment, the energy released by the impinging atoms during the sputtering process. The contribution of this last mechanism was considered negligible, since the atoms sputtered from the FeCo target have an average energy of $\approx 1 \text{ eV}$.^[59,60] They nearly have the same energy when impinging on the silk fibers as, due to the low Ar pressure (≈0.1 Pa), the energy reduction due to the thermalization with Ar atoms is negligible.^[60] For confirmation, we radiated the fibers with the electron beam of the SEM apparatus using different values of the accelerating voltage. As shown in Figure S7 (Supporting Information), the beam starts to damage the fibers when its energy is ≈ 3.4 keV, much larger than the energy of the impinging atoms.

Regarding the influence of low pressure on mechanical properties of spider silk, Ene et al.^[61] noticed that in the silk of *Trichonephila* sp. (former *Nephila* sp.), an increase in pressure led to a more organized level in the amorphous phase of the protein (which is likely to be related to an increase in strength^[42,62,63]). Thus, it is likely that the permanence in a high vacuum environment was the main cause of the experienced decrease in silk's strength. On the other hand, the metallic coating could bring about the decrease in extensibility (since its fragile nature). Overall, despite the mechanical performances of MSTs have not improved, with respect to STs ones, they are still acceptable for common applications,^[9,10,12] and also for most soft electronics components and better than common hybrid composites obtained with silkworm silk.^[19]

The study of the magnetic properties of the MSTs disclosed the magneto-mechanical effects deriving from of the interplay between the silk and the magnetostrictive FeCo layer.

The large H_C and H_{IRR} values of the FeCo_{ref} sample are an indication of the presence of internal residual stresses, induced by the growth process.^[64,65] Since FeCo is a magnetostrictive alloy, these stresses induce the appearance of a net magnetoelastic anisotropy contribution, K_E , to the total magnetic anisotropy of the film. From the analysis of the magnetic hysteresis loops measured on FeCo_{ref} with the field applied both in-plane (Figure 5a) and out-of-plane (Figure S8, Supporting Information), we estimate that $K_E \approx 8 \times 10^4$ J m⁻³, corresponding to a stress magnitude of ≈ 900 MPa (see Supporting Information Section S4 for more details). Regarding the MSTs, both SQUID and MOKE analyses showed that there is a further increase in H_C and H_{IRR} with respect to those of the reference sample FeCo_{ref}. This is consistent with an enhanced magnetic anisotropy of the MSTs.

The anisotropy increase may be determined by the existence of two possible contributions: i) a shape anisotropy term, which may originate from the particular morphology of the MSTs, i.e., an elongated structure with a curved profile^[66–68] in the form of a bundle; ii) an increase in the strength of the internal stresses, and therefore of the magnetoelastic anisotropy term, which may arise from the mechanical coupling with the silk thread. Certainly, the latter is a much more irregular structure compared to the flat Si substrate on which the FeCo_{ref} film is grown. Moreover, after the coating is deposited, the silk fibers exit the vacuum chamber and are subjected to a huge change in relative humidity, which modifies both their mechanical properties and tensional state.^[29,69]

To assess the impact of these different anisotropy contributions on the hysteretic behavior and magnetic configuration of the MSTs, micromagnetic simulations were carried out using MuMax³, a GPU-accelerated micromagnetic simulation program developed at Ghent University and exploiting the finite difference method.^[70–72]

The MST was modeled as depicted in **Figure 8**a: it is a bundle of three cylinders, each with an internal radius R_I of 500 nm, a length *L* of 400 nm, and a thickness of 100 nm. To take into account the contribution of shadowing effects related to sputtering deposition,^[51] the thickness of the magnetic layer in the grooves between adjacent fibers was reduced (Figure 8b). The saturation magnetization M_S value measured on FeCo_{ref} was used as reference. More details on the simulation methods are given in Supporting Information (Section S5).

As a first step, the micromagnetic calculation was carried out taking into account only the shape anisotropy contribution. The hysteresis loop was calculated considering that the magnetic field *H* was applied parallel to the *z* axis. The result is shown in Figure 8c. The values of H_C and H_{IRR} are 9.15 and 9.55 kA m⁻¹, respectively, less than 50% of the measured values (Table 2). This indicates that the shape term is not sufficient to account for the observed magnetic hardening of MST with respect to FeCo_{ref}.

Then, the case in which a magnetoelastic anisotropy contribution was also present was simulated. Since the exact configuration of the internal stresses in the FeCo coating was obviously unknown, we assumed that the local orientation of the

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Figure 8. a) Representation of the bundle of three cylinders, in contact with each other, with an internal radius R_1 of 500 nm, a length *L* of 400 nm, and a thickness of 100 nm. For better viewing, four replicas of the bundle are displayed. b) Actual cross section of the bundle represented in panel (a), highlighting the reduction of the thickness of the FeCo layer in the interstices between adjacent fibers. c) Hysteretic behavior of the bundle when considering only the contribution of the shape anisotropy (straight blue curve) or when also the contribution of the magnetoelastic term, having a local orientation that changes and $K_E = 8 \times 10^4$ J m⁻³, is included (green straight curve). d) Hysteretic behavior when the magnetoelastic term has an orientation parallel to the z axis and $K_{E-appl} = 3.7 \times 10^5$ J m⁻³.

magnetoelastic anisotropy axis changed while the value of K_E was the same everywhere. Assuming $K_E = 8 \times 10^4$ J m⁻³, i.e., that estimated for the FeCo_{ref} film (corresponding to a stress magnitude of 900 MPa), with respect to the previous case increased H_C and H_{IRR} (19.9 and 28.6 kA m⁻¹, respectively) are obtained (Figure 8c). Nevertheless, they are still smaller than the measured ones, which supports that the coupling of the FeCo layer with the silk leads to a value of K_E larger than that of the FeCo_{ref} film.

The micromagnetic simulations allow to calculate also magnetic configurational maps, from which maps displaying the corresponding MFM contrast can be calculated. As for the hysteresis loops, two cases were considered, i.e., without and with magnetoelastic anisotropy, namely without and with internal stresses (more details in the Supporting Information Section S6). The results (Figure S10a,b, Supporting Information) reveal that in the first case the magnetic configuration is uniform and no MFM contrast is visible, while a magnetic contrast of variable sign appears at the sides of the fibers when the magnetoelastic anisotropy is included in the calculation. This last finding is in line with the experimental results of Figure 6b and therefore confirms the presence of a non-uniform local stress pattern in the FeCo coating.

When the MSTs are subjected to a tensile strain ($\varepsilon = 0.025$), differences in the hysteresis loop shape (Figure 5c) and in the MFM map (Figure 6d) are clearly observed with respect to the unstrained case, indicating the existence of a drivable magnetomechanical coupling between the silk core of the thread and the magnetostrictive FeCo coating. To simulate the influence of the strain on the magnetic properties of the MST, we needed to estimate K_F . However, the evaluation of the magnitude of the actual applied stress, which produces the strain ε = 0.025, is not straightforward. In fact, when a strain is applied to a flexible substrate covered by a metallic layer, the strain may not be uniform along the thickness.^[56,73] The applied stress can be roughly estimated as $\sigma_{appl} = E_{FeCo} \times \epsilon$, where E_{FeCo} is the Young modulus of FeCo. Assuming $E_{FeCo} = 165$ GPa, i.e., the value expected for thin FeCo layers,^[74,75] we obtain $\sigma_{appl} = 4.1$ GPa. This value is ≈4.5 times larger than that of the internal stresses (i.e., 900 MPa) used in the previous simulations of the unstrained MST. Therefore, the micromagnetic calculations were carried out assuming that the magnetoelastic anisotropy term associated to σ_{appl} , i.e., $K_{E-appl} = 3.7 \times 10^5$ J m⁻³, is the leading one and the contribution related to the internal stresses can be disregarded.

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The obtained hysteresis loop is reported in Figure 8d, H_C and H_{IRR} are 255 kA m⁻¹ and 279 kA m⁻¹, respectively. Hence the two parameters increase with increasing ε , an effect confirmed by the experiments, although the measured values of H_C and H_{IRR} are definitely lower (Table 2) probably because σ_{appl} is overestimated.

The calculated MFM map, displayed in Figure S10c (Supporting Information), shows just a feeble magnetic contrast. Therefore, the application of a tensile stress to MST results in an overall more uniform magnetic configuration, as experimentally observed (Figure 6d).

Finally, the magnetic actuation of MST was investigated by measuring the tensile force generated on the thread when a group of magnets was approached. The generated load, and also the corresponding stress, were larger than those produced by typical biomedical magnetic actuators.^[76,77] Moreover, MST was repeatedly bent under actuation with a degree desirable in magnetic actuators for soft robotics applications (Video S2, Supporting Information).^[78] For example, in Gao et al.,^[79] flexible magnetic microelectrodes generated a stress of about a few MPa when exposed to a variable magnetic field, comparable to what was here achieved with only one thread, thus the MSTs display properties that are suitable for such applications.^[80] These results highlight the potentiality of using hybrid systems of this kind as basic components for magnetic actuators.

4. Conclusions

Soft robotics and electronics are fast-moving fields, in which every day new materials emerge, as well as new needs. Among these, the necessity of having flexible electrical fabrics that retain the mechanical efficiency and the electrical properties is commonly highlighted. The magnetic properties are an added value that can be used to generate actuation, improve the interface with the device, perform sensing, and store information. To achieve such needs, new types of highly performant composite fibers are to be designed.

In this work, we present a new spider-silk based material with a strong multifunctional nature. Despite the treatment, the spider silk fibers nearly preserved their natural mechanical properties, but also gained additional functionalities, namely stress-sensing magnetic properties, thanks to a magneto-mechanical coupling between the silk core of the thread and the magnetostrictive FeCo coating, and a strain-dependent electrical conductivity. This hybrid system has been here characterized from mechanical, magnetic, and electrical point of views, providing a solid proof of concept of this functional engineered spider silk. This fiber could be used as a component in soft electronics/robotics and sensing composites nearly as it is, or used as a proof for further investigations with other type of fibers including the relevant example of artificial spider silk, which can be now produced at large scale.^[81]

5. Experimental Section

Silk Collection: The spider silk studied in this work was produced by Cupiennius salei (Keyserling 1877).^[41] The spiders were kept in different

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glass or plastic terrariums and fed with a weekly diet of insects (*Blaptica dubia* or *Acheta domestica*). All the terrariums were set in a room with controlled environmental parameters. Each terrarium was provided with a small refuge by considering the needs of the animal, according to the Italian regulation on animal protection and EU Directive 2010/63/EU for animal experiments. The spider, during its walking inside the terrarium, continuously produced dragline silk threads (Figure 1a), which were composed by at least two silk fibers (Figure 1b). These threads, whose length was of approximately 20 cm, were collected and consequently cut into smaller pieces and then prepared for further characterization.

Spider Silk Coating: The samples were prepared by following the procedure reported by Blackledge et al.^[38] Briefly, each ST was cut into pieces of the desired length using scissors, and each specimen was then placed on a cardboard frame provided with a window of 0.75 cm imes 0.75 cm and fixed with a double-sided tape (Figure 1c). To obtain the MSTs, the STs fixed in the cardboard frame were coated with a 100 nm thick magnetic layer made of a FeCo alloy (Figure 1d,e). The magnetic layer was deposited with a custom-made high-vacuum dc magnetron sputtering apparatus^[82] in Ar atmosphere (Ar pressure \approx 0.1 Pa, base pressure \approx 10⁻⁵ Pa) using a high purity FeCo sputtering target. The nominal value of the thickness of the films was measured with a quartz microbalance system based on 6 MHz gold plated crystal, a Vaqtec Oscillator Kit, and an MS-9150 Metex Universal System. During the deposition process, which involved an overall permanence in high vacuum conditions of ≈50 minutes, the cardboard frame was placed on a rotating sample holder so to improve the layer homogeneity. As a reference magnetic sample, a 100 nm thick FeCo film was also deposited on a planar naturally oxidized silicon substrate, under the same experimental conditions adopted for coating the STs. This reference film was labeled as FeCo_{ref}. The transformation of STs in MSTs involved two steps, namely the permanence in a high vacuum chamber and the deposition of the FeCo coating. Therefore, as a control, an additional set of samples, VSTs, was also prepared. VSTs were obtained by exposing the STs to a high vacuum stage comparable to that used for the preparation of the MSTs, i.e., they were kept at 10^{-5} Pa for ≈ 50 min.

Scanning Electron Microscopy: For the SEM morphology characterization, an FE-SEM Zeiss – 40 Supra was used. Regarding the STs, before the observation they were coated with a Pt/Pd (80:20) layer (Quorum technology, Q150T) having a thickness of \approx 5 nm. All the SEM observations were performed after the tensile tests by collecting both secondary and backscattered electrons.^[83,84] EDXS analysis was performed on MSTs using an EM-30 COXEM. The spectra were obtained at 20 kV, at a magnification of 10⁴. The measurements were performed 2 months after the coating of the threads, so to test the durability of the coating.

Electrical Conductivity: The electrical conductivity measurements were performed on MSTs with the four-point collinear probe method, by fixing the intensity of the current flowing in the sample and measuring the potential drop. The current generator was a Keithley 2450 Sourcemeter and an Agilent 34401A Digital multimeter was used as voltage probe. Electrical contacts between the instruments wires and the MST were made possible using silver-loaded paint. For these measurements, the MSTs were detached from the cardboard frame and fixed on a sample holder that, thanks to an endless screw, allowed to extend the length of the samples. In this way, the measurements could be performed both in zero strain and in strained conditions.

Mechanical Properties: Tensile tests were carried out using a nanotensile machine (Agilent® technologies T150 UTM) with a cell load of 500 mN, nominal declared sensitivity of 10 nN for the load, and 1 Å for the displacement in the dynamic configuration. The strain rate was 1% s⁻¹ (gauge length of 7.5 mm) with a frequency load of 20 Hz. Before mounting the sample, the number of fibers per thread and the diameter of each fiber were measured with an optical microscope (Zeiss Axiotech and Axiovert) and ImageJ software analysis.^[85] For each group of STs, at least ten samples were tested, and the mean values \pm standard deviation of strength (MPa), strain at break (mm mm⁻¹), toughness modulus (MJ m⁻³), and Young's modulus (GPa) were

calculated from the engineering stress–engineering strain curves.^[22] Briefly, for each sample the engineering stress was obtained by dividing the value of the applied force by the initial cross section of the thread. This was calculated as the sum of the cylindrical cross sections of each fiber that composes the thread, whose diameter was measured by means of light microscopy.^[50] The engineering strain was obtained by dividing the displacement by the initial gauge length. Making reference to the engineering stress–engineering strain curve, the Young's modulus was evaluated as the slope of the initial (steepest) part of that curve whilst the toughness modulus as the area below the entire curve. The tensile tests were performed 2 weeks after the samples preparation.

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Statistical Analysis: The values of the ultimate strength were analyzed through the support of the software Mathematica so to obtain the Weibull parameters through the maximum likelihood method.^[22,43] One-way analysis of variance (pairwise comparison) was performed to compare the mechanical properties, with a significance level of 5%. The two-tailed *p*-value were computed with the support of Matlab as previously described.^[22]

Magnetic Characterization: The magnetic properties of the samples were investigated by a SQUID Quantum Design MPMS-XL magnetometer operating in the 5–300 K temperature range (maximum applied field 4 MA m⁻¹, sensitivity 10^{-10} A m²).^[86]

The magnetic behavior of the MSTs was also studied with a MOKE magnetometer, using the transverse configuration setup and the intensity modulation technique.^[86,87] In this case, the maximum applied field was 160 kA m⁻¹. In more detail, the direction of the MST was kept parallel to that of the magnetic field and both of them were orthogonal to the scattering plane. In this configuration, *p* polarized light produced by a He-Ne laser (wavelength $\lambda = 632.8$ nm) was focused onto the MST and the light diffused by the sample was collimated on a Thorlabs PDA55 amplified silicon detector. For the MOKE measurements, the samples were installed using the same sample holder adopted for conductivity measurements.

Atomic Force and Magnetic Force Microscopy: AFM and MFM characterizations were performed with a Bruker Multimode V Nanoscope 8 microscope, equipped with CoCr coated MESP-HR tips. Images were taken in air with the samples at their magnetic remanence, with the tip magnetized along its axis (vertical direction). During each image acquisition, the height channel was acquired in pass 1 in intermittent contact mode, and the magnetic channel was acquired in pass 2 at a constant lift scan height of 35 nm (~1 Hz acquisition, 384 lines). For these measurements, the samples were installed using the same sample holder adopted for MOKE measurements.

Magnetic Actuation: The mechanical response of the MSTs was evaluated through a custom-made setup. A nanotensile machine (Agilent technologies TI50 UTM) was used to measure the load response of the samples and a commercial set of cubic (lateral side of 5 mm) Nickel plated N42 NdFeB magnets (by Webcraft GmbH) was used to expose the MST to a non-uniform *B* field, so as to apply a drag force to the sample.^[88] The *B* intensity was measured using a FW-Bell 9500 Gaussmeter using a 1-axis Hall probe.

Each MST was set on a 0.5% level of strain and held for 120 s. After the relaxation, a static configuration was kept (the grips held the sample by measuring its mechanical response) and the MST was gradually exposed to the magnetic field by slowly approaching the cubic magnets to the MST. Their relative distance was measured by means of a Sony Camera HD. This procedure was repeated several times for each MST sample and for STs, as well, that were used to have a reference background signal, which was then subtracted from MST data.

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

F.S. and G.G. contributed equally to this work. G.G. and F.S. conceived the idea and prepared the samples; G.G. performed the mechanical, SEM, and actuation characterizations; L.D.B., M.C., and F.S. carried out the magnetic study; G.G., F.S., and L.D.B. wrote the original draft. N.M.P., G.G., and F.S. acquired the funding and supervised the study. All the authors approved the final version of the manuscript.

Data Availability Statement

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

Keywords

AFM/MFM analysis, hybrid materials, magnetic microtubes, magnetic properties, mechanical properties, sensor applications, SQUID magnetometry

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Supporting Information

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Magnetostrictive and Electroconductive Stress-Sensitive Functional Spider Silk

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Supporting Information

Magnetostrictive and Electroconductive Stress-Sensitive Functional Spider Silk

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S1. Energy dispersive X-ray spectroscopy (EDXS)



Figure S1. EDXS spectrum collected on a MST sample using a COXEM desktop Scanning Electron Microscope with the EDX detector; the data were acquired at 20 kV with a magnification of 10000. The presence of the Fe and Co peaks is a clear indication of the presence of the magnetic coating.

S2. MST electric and magnetic properties under cyclic loading

Electric and MOKE measurements were also performed on the MSTs under cyclic tensile loadings. Each sample was subjected to 5 loading cycles, with ε starting from 0, reaching a given ε_{MAX} value and then going back to 0.

Regarding electrical measurements, for a better comparison the data are displayed as relative variations of resistance, $\Delta R/R_0$: $\Delta R = R - R_0$, where R_0 is the initial value of the resistivity and R the current one. In **Figure S2**a, the $\Delta R/R_0$ values measured during the cycles of four different samples are presented using coloured symbols (full symbols are the values measured when ε_{MAX} is applied for the first time; open symbols are the values measured at the end of the last cycle, at $\varepsilon = 0$); black symbols refer to the data presented in Figure 3b and discussed in Section 2.2, that correspond to the monotonic loading of a sample, and are included here just for comparison. Each sample was measured under a different ε_{MAX} value. For $\varepsilon_{MAX} = 0.007$ (red) and $\varepsilon_{MAX} = 0.01$ (green), the final $\Delta R/R_0$ is ~ 5 % smaller than that measured when first applying ε_{MAX} . Differently, for $\varepsilon_{MAX} = 0.025$ (light blue) and $\varepsilon_{MAX} = 0.045$ (blue), $\Delta R/R_0$ is very close to that measured when first applying ε_{MAX} . This indicated that, even under cyclic loading, the FeCo coating was not stripped. However, the electrical behavior was not fully reversible, which suggests that the loading process induced defects in the FeCo layer.

Figure S2b shows the magnetic hysteresis loops recorded by MOKE on a MST sample before and after the 5 cycles of loading at $\varepsilon_{MAX} = 0.025$, namely the same value of engineering strain applied during the measurement of the loop presented in Figure 5c. The shape of the loops was quite similar. After the repeated loading, an increase of H_C of just ~ 8 % was experienced. It is worth reminding that the value of H_C measured under strain was ~ 28% higher than that measured in the unstrained sample (Figure 5c), due to the tensional state of the FeCo coating, as discussed in the main text. Therefore, the results in Figure S2b supported the same conclusions reached through the electrical measurements, i.e. they indicated that the coating was not stripped after repeated loading cycles, although the initial properties were not fully recovered, possibly due to the formation of cracks.

The sputtering deposition method and the use of Fe and Co based alloys favor the adhesion of the metallic coatings on polymeric substrates,^[1,2] so a strong FeCo coating – silk fibers interaction may be expected. On the other hand, as discussed in section 3, the grooves between adjacent fibers may favor cracks formation.



Figure S2. (a) Relative resistivity variations $\Delta R/R_0$ vs. ε . Coloured symbols refer to four MST samples subjected to cyclic loading up to a maximum value of ε (ε_{MAX}). The used ε_{MAX} values are: 0.007 (red), 0.01 (green), 0.025 (light blue), 0.045 (blue); full symbols are the $\Delta R/R_0$ values measured when applying ε_{MAX} during the first cycle and open symbols are the values measured at the end of the last cycle, at $\varepsilon = 0$ (full and open symbols corresponding to the same loading process are connected by arrows). Black symbols are the same data already presented in Figure 3b and discussed in Section 2.2, that correspond to the monotonic loading of a sample; they are included here just for comparison (the black line is a guide to the eye). (b) Magnetic hysteresis loops recorded by MOKE on a MST sample before (black) and after (blue) the cyclic loading.

Sample	ST	MST	VST
ST		0.5823	0.000074
MST	0.5823		0.0006
VST	0.000074	0.0006	

Table S1. p-values of the pairwise comparison of the strain at break.

 Table S2. p-values of the pairwise comparison of the strength.

Sample	ST	MST	VST
ST		0.0171	0.0117
MST	0.0171		0.6585
VST	0.0117	0.6585	

Table S3. p-values of the pairwise comparison of the Young's modulus.

Sample	ST	MST	VST
ST		0.8957	0.0642
MST	0.8957		0.037
VST	0.0642	0.037	

Table S4. p-values of the pairwise comparison of the toughness modulus.

Sample	ST	MST	VST
ST		0.037	0.0513
MST	0.037		0.7134
VST	0.0513	0.7134	



Figure S3. Experimental dependence of Strength (a), Young's modulus (b), and Toughness modulus (c) on the diameter of the threads for the three types of threads investigated in the manuscript: as-prepared silk thread ST, magnetic silk thread MST, and vacuumed silk thread VST. For each group, the lines represent the best fit to a linear dependence.



Figure S4. a) Representative roughness profile recorded on the surface of a MST along a straight line path, as indicated in the b) AFM map.

S3. Evaluation of the magnetic field produced by the commercial magnets

The magnetic field generated by the commercial magnets was evaluated using the ANSYS[®] Electromagnetics Suite Release 2020 R2, a finite element software. The six cubic (lateral side of 5 mm) Nickel plated N42 NdFeB magnets were arranged as displayed in **Figure S5**a, and their magnetic configuration was set to be equal to the one described in the same figure. For the magnetic induction *B* calculation, we used the Maxwell 3D magnetostatic solver. We assigned the magnets a remanence value equal to 1.05 MA m⁻¹, corresponding to the maximum value reported for N42 NdFeB on the documentation available at the producer website.^[3] In Figure S5b, left panel, the *B* intensity evaluated on the grey plane displayed in Figure S5a is presented. The intensity profile changes rapidly in space, in particular as the distance from the front side of the magnets increases (green arrow, Figure S5a), thus indicating that *B* configuration is strongly non-uniform. The experimental values of the *B* dependence as a function of the distance from the magnets, as measured across the green arrow, are presented in **Figure 7c**. In Figure S5b, right panel, the *B* orientation on the grey plane is displayed. *B* is always parallel to the plane and, along the green arrow, *B* is perpendicular to the arrow, i.e. *B* is always parallel to the front side of the magnets.



Figure S5. a) Representation of the north (N / red) and south (S / blue) poles configuration of a single commercial magnet (upper part), and of the group of magnets used for the experiment (lower part). This panel is similar to the one presented in Figure 7b of the main text, and also includes a gray rectangle (with a longer side of 4 cm and a shorter side of 3 cm) that represents the area where the magnetic field H was evaluated, as explained in the text. b) Maps showing the intensity (left side) and the orientation (right side) of the magnetic induction calculated on the gray rectangle displayed in panel a). The green arrow represented in the two maps corresponds to the green arrow displayed in panel a).

As shown in Figure 7a, during actuation measurements the front side of the magnets was always kept parallel to the MST, so H was parallel to the MST orientation, namely to the FeCo coating. Therefore, in this configuration, the H orientation favors a uniform MST magnetic configuration, so to increase the intensity of the applied force.^[4]



Figure S6. Reference results of cyclic magnetic actuation experiments performed on the same MST sample. During each experiment, the magnets (Figure S5a) where approached to the sample following the same linear trajectory (green line in Figure S5a) but with a different speed, thus the stress time dependence changes. The maximal stress values corresponding to the different approaches, detected for a sample to magnets distance of ~ 0 cm, are always close to the 10 MPa value, thus showing that the response of the material is reproducible.



Figure S7. SEM images showing the effect of the SEM electron beam on the silk fibers when the accelerating voltage of the beam was equal to a) 3.2 kV, b) 3.3 kV, and c) 3.45 kV. Significant damage is observed at 3.45 kV.

S4. FeCo magnetic properties

As observed in **Figure 5**a, the coercivity, H_c , of the FeCo_{ref} sample is larger than that expected for bulk alloys, that is of the order of 0.1 kA m⁻¹.^[5] The origin of the high H_c value may be due to the presence of a residual mechanical stress, σ , induced by the sputtering growth process,^[6,7] and to the fact that the FeCo alloy displays magnetoelastic properties. Indeed, if a magnetoelastic polycrystalline film is subjected to a mechanical stress, this will affect the magnetization reorientation process of the film through the development of a magnetoelastic anisotropy energy density contribution, E_{ME}, expressed as

$$E_{ME} = \frac{3}{2} \lambda_S \,\sigma \sin^2 \theta = K_E \sin^2 \theta \tag{1}$$

where λ_s is the saturation magnetostriction, θ is the angle between the stress axis and the magnetization, and K_E is the magnetoelastic anisotropy energy density.^[8] For FeCo, $\lambda_s \sim 60 \times 10^{-6}$.^[5] In this case, if a tensile (positive) stress is applied along a specific direction in the film plane, the magnetic behavior of the sample becomes anisotropic. Indeed, the E_{ME} term is minimum when the magnetization is parallel to that direction, that thus becomes an easy magnetization axis, whilst a direction perpendicular to that becomes a hard magnetization axis. The opposite occurs for a compressive (negative) stress. On the other hand, if the stress is uniform in the plane of the film, an isotropic behavior is expected. In particular, due to the contribution of the magnetoelastic anisotropy energy, a higher H_C value is predicted with respect to the $\sigma = 0$ case.^[9]

The measured in-plane hysteresis magnetization loops display an in-plane isotropic behavior (Figure 5a), with a squared shape and a high remanence $M_R = M(H=0)/M_S \sim 0.88$. Therefore, we expect that the magnetization lies in the plane of the film, and that the residual stress is uniform and positive. To check this hypothesis, we measured the magnetic hysteresis loop by applying a magnetic field perpendicular to the film plane, i.e. in the out-of-plane direction, to estimate the in-plane magnetic anisotropy K_{IP} .^[10] Indeed, the anisotropy field $H_K = 2 K_{IP}/M_S$ corresponds to the knee of the out-of-plane hysteresis loop. For FeCo_{ref}, K_{IP} depends on both the shape and the magnetoelastic anisotropy. If only the former is present, K_{IP} equals to the magnetic shape anisotropy, K_S , that for a thin film is $K_S = -(1/2) M_S^2$.^[4] In our case, $K_S = -1.9 \times 10^6$ J m⁻³, and $H_K = 2 |K_S|/M_S \sim 1.75$ MA m⁻¹. The out-of-plane magnetic hysteresis loop is presented in **Figure S8**, and $H_K \sim 1.81$ MA m⁻¹, higher than 1.75 MA m⁻¹. Thus, we may conclude that also for the magnetoelastic anisotropy the out-of-plane direction is a hard axis, confirming the initial hypothesis that the residual stress is tensile. As $K_{IP} = K_E + K_S$,^[4] $|K_E| = |K_{IP} - K_S| \sim 8 \times 10^4$ J m⁻³, and, using equation (1), $\sigma \sim 900$ MPa.



Figure S8. SQUID magnetic hysteresis loops measured at room temperature on FeCo_{ref} with the external field applied perpendicular to the plane of the film.

S5. Micromagnetic simulations

Micromagnetic simulations were carried out using MuMax³.^[11-13] The simulations were performed so to obtain information on both the hysteretic behavior and the magnetic configuration of three different geometries: G1, a square with a lateral size of 1 μ m, with a thickness of 100 nm; G2, a single cylinder, with an internal radius R_I of 500 nm, a length L of 400 nm, and a thickness of 100 nm (**Figure S9**a); G3, a combination of three cylinders, each with $R_I = 500$ nm, L = 400 nm and a thickness of 100 nm (Figure S9b). The three geometries represent the FeCo_{ref} sample (G1), a single silk fiber covered by a 100 nm thick FeCo layer (G2), and a bundle, made of three fibers, covered by a FeCo layer (G3). Regarding G3, to take into account the contribution of shadowing effects related to sputtering deposition,^[14] in the grooves between adjacent fibers the thickness of the magnetic layer has been reduced (see the map in **Figure 8**b).

In the used reference frame (Figure S9a), for G1 the *x* axis was perpendicular to the film plane and *y* and *z* axes were parallel to that. For G2 and G3, the *z* axis was parallel to the symmetry axis of the cylinders, whilst *x* and *y* axes were orthogonal to that. The simulated geometries were discretized using a grid of identical cubic cells in which the magnetization was assumed to be uniform. As a reference value for the saturation magnetization M_S we used that measured on sample FeCo_{ref} (1.75×10^6 A m⁻¹, see Section 2.4). Regarding the lateral size of the cells, in general its value is chosen of the order of the ferromagnetic exchange length, l_{ex} , of the considered ferromagnetic material.^[15,16] l_{ex} is defined as (2)

 $A_{ex}/(\mu_0 M_S^2))^{0.5,[17,18]}$ where A_{ex} is the exchange stiffness. For FeCo, $A_{ex} = 1.6 \times 10^{-11}$ J m^{-1,[19,20]} and $l_{ex} \sim$ 3 nm. In our case, as we wanted to use the same cell size for the three geometries, due to hardware memory constraints we had to limit the total number of cells and therefore a cell size of 10 nm was used. In the case of G2 and G3, to prevent a possible contribution from the 'staircase' surface due to the use of coarse grained cells, the MuMax³ edgesmooth option was used. To avoid finite size effects, the calculations were carried out using periodic boundary conditions: G1 was replicated along both *y* and *z* directions, G2 and G3 were replicated along the *z* direction. In this way, the comparison between G1 and G2 allows to estimate the contribution of the curved geometry to the magnetic properties, whilst the comparison between G2 and G3 allows to point out possible effects on the magnetic properties related to the bundle structure.

For the calculations on the three geometries, the magnetic field H was applied parallel to the z axis. Actually, a 3° tilt was introduced whilst performing the calculations so to mimic the experimental conditions, as it is difficult to apply the magnetic field precisely parallel to a given direction. For each case, the micromagnetic calculations were performed over 5 equivalent replicas, and the presented hysteresis loops are obtained as an average over the 5 resulting ones.

The results obtained when just the shape anisotropy K_S was included in the calculation are presented in Figure S9c. For G1, as expected, H_C is negligible and the magnetization rotation process is sharp, while for G2 $H_C \sim H_{IRR} \sim 7.96$ kA m⁻¹. For G3, $H_C \sim 9.15$ kA m⁻¹, $H_{IRR} \sim 9.55$ kA m⁻¹, the magnetization reversal starts with a smooth decrease of the magnetization followed by a sharp rotation. Hence, when comparing just the magnetostatic contribution, i.e. the effect of the shape anisotropy, the main difference is observed when moving from G1 (plane film) to G2 (single cylinder), whilst passing from G2 to G3 (bundle structure) does not bring about significant modifications.

We also tried to estimate the contribution to H_C and H_{IRR} that may stem from the presence of local stresses, in the FeCo layer, induced by the interaction with the silk threads, as described in section 3. We made the hypothesis that the stresses orientation could randomly change along the coating and that the stresses intensity was equal to that detected for FeCo_{ref}, ~ 900 MPa (section S4), so $K_E = 8 \times 10^4$ J m⁻³. The simulation was performed for geometry G3, as that is the one that more closely resembles the MST configuration. The results are presented in Figure 8c and, as it can be observed, $H_C \sim 19.9$ kA m⁻¹ and the *H* range where the magnetization reversal takes place has a width of about 15.9 kA m⁻¹.

For the strained case, we used the hypotheses presented in section 3, namely that: (i) the strain felt by the FeCo layer is equal to that applied to the MST; (ii) the strain is uniform through the thickness; (iii) no cracks are developed. Due to that, as explained in section 3 σ = 4.1 GPa, with an orientation that is parallel

to the MST length. The intensity of the corresponding uniaxial magnetic anisotropy is $K_{E-appl} = 3.7 \times 10^5$ J m⁻³. Overall, as both σ and K_{E-tens} are ~ 4.5 times larger than the corresponding values used for the unstrained case, we may consider that, when the tensile strain is applied, the induced stress, and the corresponding anisotropy, become the leading terms.

The resulting hysteresis loop is presented in Figure 8d. The effect of the tensile stress is very pronounced, as both H_C and H_{IRR} are much higher with respect to the unstrained case, as their values are 255 kA m⁻¹ and 279 kA m⁻¹, respectively.



Figure S9. 3D representations of two of the simulated geometries: a) G2, a single cylinder, with internal radius $R_I = 500$ nm, a length L = 400 nm and a thickness of 100 nm; b) G3, made of three cylinders, in contact with each other, having $R_I = 500$ nm, L = 400 nm and a thickness of 100 nm. For better viewing, 4 replicas of G2 and G3 are displayed. G3 is also presented in Figure 8a. c) Hysteretic behavior of the

different geometries presented in the text, G1 (blue straight line), i.e. a 100 nm thick plane FeCo layer, G2 (red straight line) and G3 (black straight line), when the magnetic field H is parallel to the z axis.

S6. Simulation of the MFM maps

In Section 2.5, the comparison between the MF maps collected on a MST, both in unstrained ($\varepsilon = 0$) and in strained ($\varepsilon = 0.025$) conditions, is presented. To explain the difference in magnetic contrast between these two configurations, we made the hypothesis that that is due to the contribution of the stress induced magnetic anisotropy that developed in the strained state. We tried to verify that hypothesis, so we computed and compared the MFM maps that corresponded to the $\varepsilon = 0$ and $\varepsilon = 0.025$ configurations. The analysis was based on the micromagnetic approach presented in Section S5 and was applied to geometry G3, as that more closely resembles the MST. In more detail, the MFM signal was related to the second derivative of the vertical component of the stray field generated by G3 and calculated with respect to the vertical direction.^[21] The stray field was computed through the MuMax³ software from the magnetization map evaluated at the magnetic remanence. The second derivative was calculated at a distance of 35 nm from G3 surface, so to adopt the same conditions used for MFM measurements (see Section 5.8). To evaluate the magnetization maps corresponding to the unstrained and to the strained case, we used the same approach presented in Section S5. For reference, also the MFM map corresponding to the absence of magnetoelastic contributions, i.e. when just the shape anisotropy is included in the calculation, was calculated.

The comparison between the simulated MFM maps corresponding to the three described configurations, $K_E = 0 \text{ J m}^{-3}$, $K_E = 8 \times 10^4 \text{ J m}^{-3}$, $K_{E\text{-appl}} = 3.7 \times 10^5 \text{ J m}^{-3}$, are presented in **Figure S10**a, S10b, and S10c, respectively, and discussed in section 3.



Figure S10. Comparison between the simulated MFM maps evaluated on the bundle of 3 cylinders (described in Figure S9b) when: a) only the presence of the magnetic shape anisotropy is considered; b) also the magnetoelastic anisotropy is included, having a local orientation that changes while $K_E = 8 \times 10^4$ J m⁻³; c) the magnetoelastic anisotropy has an orientation parallel to the *z* axis and $K_{E-appl} = 3.7 \times 10^5$ J m⁻³. In panels a), b) and c), for better viewing, the maps were replicated 4 times: the horizontal straight lines represent the separation between the different copies. The four arrows included at the bottom of panels a), b) and c) are a reference to the four vertical dashed lines displayed in panel d), that are related to the morphology of the bundle: lines 2 and 3 correspond to the borders of the top fiber, line 1 to the left border of the fiber located at the bottom, on the left, and line 4 to the right border of the fiber located at the bottom.

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