

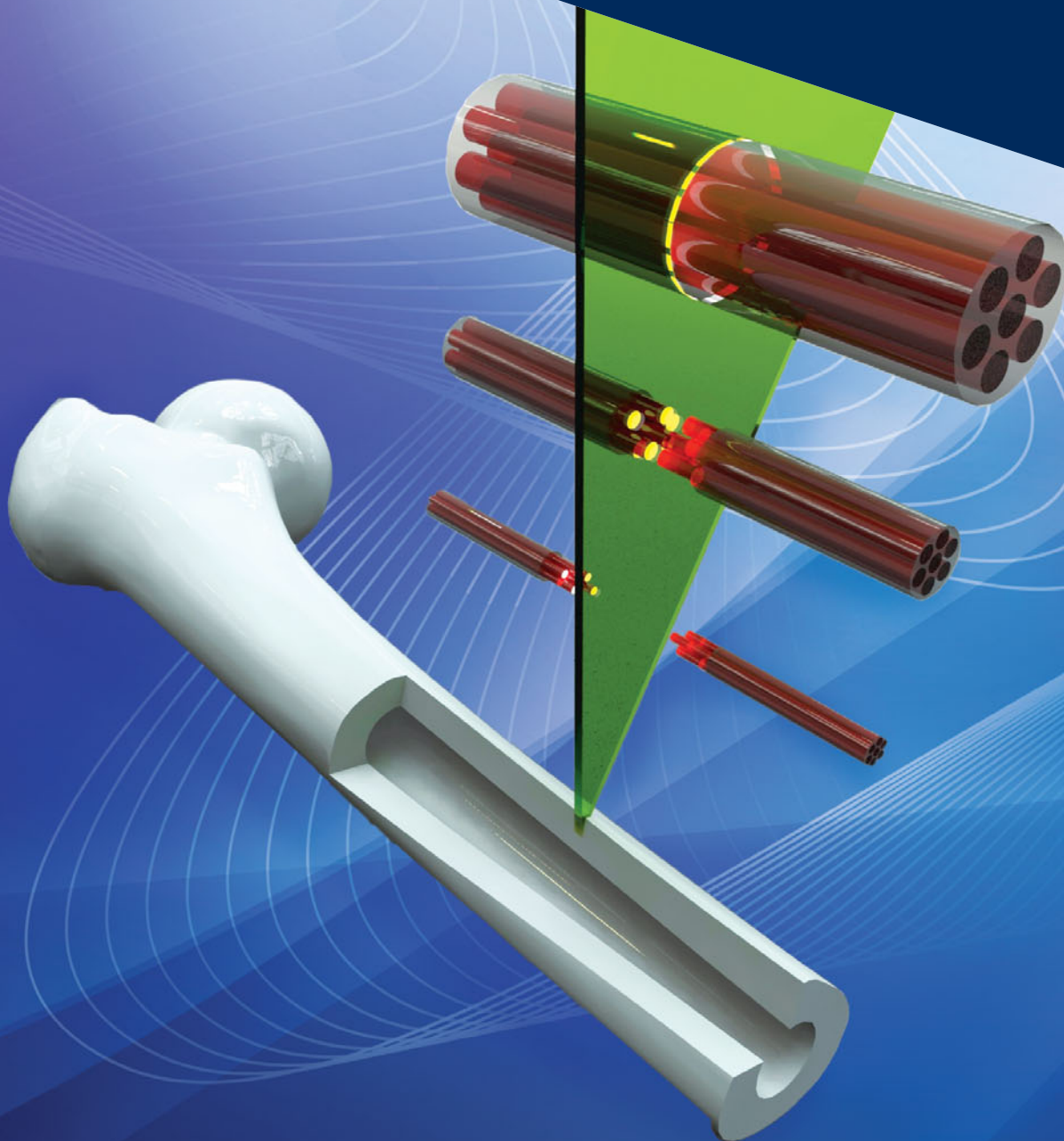


Journal of
MATERIALS RESEARCH

VOLUME 30 • NO 1
JANUARY 14, 2015

FOCUS ISSUE

Soft Nanomaterials



Fatigue of self-healing hierarchical soft nanomaterials: The case study of the tendon in sportsmen

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(Received 7 July 2014; accepted 21 October 2014)

One of the defining properties of biological structural materials is self-healing, i.e., the ability to undergo long-term reparation after instantaneous damaging events, but also after microdamage due to repeated load cycling. To correctly model the fatigue life of such materials, self-healing must be included in fracture and fatigue laws, and related codes. Here, we adopt a numerical modelization of fatigue cycling of self-healing biological materials based on the hierarchical fiber bundle model and propose modifications in Griffith's and Paris' laws to account for the presence of self-healing. Simulations allow us to numerically verify these modified expressions and highlight the effect of the self-healing rate, in particular, for collagen-based materials such as human tendons and ligaments. The study highlights the effectiveness of the self healing process even for small healing rates and provides the possibility of improving the reliability of predictions of fatigue life in biomechanics, e.g., in sports medicine.

I. INTRODUCTION

One of the distinctive characteristics of biological structural materials is their ability to autonomically repair progressive damage, or in other words to achieve self-healing.^{1,2} Typical examples are skin, bone or tendons, where the long term reparation occurs as a result of an initial damaging event.³ Drawing inspiration from these natural systems, self-healing artificial materials have also been designed and produced, using diverse approaches and various constituents, from systems based on “microcapsules” containing a healing agent,^{4,5} to “vascular-based” systems,^{6,7} to “molecular-based” systems.^{8,9} In particular, self-healing was found to be particularly effective in increasing the fatigue life of composites^{8,10} and polymers,¹¹ where up to 90% recovery of fracture toughness was achieved. A review of approaches to self-healing in artificial materials can be found in Ref. 12, while a review of numerical

modeling methods applied to such systems is given in Ref. 13.

In biological materials, damage generally evolves as a consequence of cyclic loading during the whole lifetime of a particular tissue. Tendons and ligaments are typical examples. Their function is to transmit forces between bones and muscles or bones and other bones, and are constituted essentially by type I collagen fibers.¹ As for other biological structural materials, they display a hierarchical structure that encompasses various size scales, ranging from collagen molecules (nanometer scale), to microfibrils, to fibrils, to fibers, to fiber fascicles, and to the final tissue itself (at cm scale).¹⁴ Thus, tendons and ligaments can be considered an example of “soft nanomaterials”. From a mechanical point of view, they can be modeled as bundles of viscoelastic fibers organized in a hierarchical structure, cyclically loaded in the fiber direction in uniaxial tension. Thus, a fiber bundle model-like approach¹⁵ with the inclusion of hierarchy and self-healing is ideally suited to simulate the mechanical behavior of these biological structures. In previous work, we introduced such a hierarchical fiber bundle model (HFBM)^{16,17} coupled with self-healing¹⁸ to study the effects of material regeneration on the strength and toughness of hierarchical composite materials.

As mentioned above, damage to tendons and ligaments can be caused by macrotraumas but more often by

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This author was an editor of this focus issue during the review and decision stage. For the *JMR* policy on review and publication of manuscripts authored by editors, please refer to <http://www.mrs.org/jmr-editor-manuscripts/>.

DOI: 10.1557/jmr.2014.335

repeated exposure to lower magnitude stresses, i.e., fatigue. In the case of humans, healthy individuals are estimated to walk approximately 1–1.5 million strides per year, and in sporting activities so-called “tendon overuse injuries” are estimated to be about 30–50% of all sports-related injuries.¹⁹ Clearly, however, tendon inflammation, degeneration, and ultimately fatigue life depend on the stress level to which they are subjected. For example, cyclic loading at a 40% level of the ultimate tensile strength (UTS) would typically lead to failure after approximately 8500 cycles, whilst at 20% of the UTS, the fatigue life would be of the order of 300,000 cycles (i.e., about four months of normal walking activity).^{19,20} This type of prediction, however, is based on the results from in vitro mechanical tests on tendons,²¹ whilst self-healing and remodeling effects are present in vivo and cannot be neglected in order not to underestimate fatigue life. Thus, a numerical model which is able to estimate the fatigue life of tendons starting from known mechanical properties and including self-healing effects would be of considerable interest to help, e.g., in the diagnosis and prediction of overuse injuries. In this paper, we extend the above-mentioned HFBM to simulate cyclic loading and thus fatigue, and study the influence of self-healing on biological materials such as tendons and ligaments.

The paper is structured as follows: In Sec. II, the theoretical influence of self-healing on fracture stress and fatigue life is discussed; In Sec. III, the numerical approach is presented; In Sec. IV, calculation and simulation results are compared and discussed. Conclusions conclude the paper.

II. FRACTURE STRESS AND FATIGUE LIFE LAWS IN THE PRESENCE OF SELF-HEALING

We wish to analytically estimate the scaling of fracture stress and fatigue life in self-healing materials as a function of their healing rate η . Self-healing is a function of time, but also of damage level, since it is triggered by damage, increases with damage, and stops if no further damage occurs, albeit with some time delay. Here, we consider loading to be slow enough for the system to be described in the quasistatic regime, so that dependence with respect to time can be neglected, and only dependence with respect to the damage level is significant. Thus, the healing rate η , which is a function of time and damage level, can be defined as the ratio between the “healed” volume portion of the material and the “damaged” volume portion in a given fixed time interval. As a first approximation, we will consider η constant.

We first consider the relation for the scaling of the fracture stress σ_F in an infinite linear elastic plate with a central crack of length $2a$ and subjected to uniaxial tension perpendicularly to the crack (Griffith’s case), which according to Linear Elastic Fracture Mechanics (LEFM)²² is $\sigma_F = K_{IC}/\sqrt{\pi a}$, where K_{IC} is the critical

stress intensity factor, or fracture toughness, for mode I crack propagation. If we now consider that the effect of self-healing is to limit crack growth, we can assume, as a first approximation, that the crack length term a is modified to $a(1 - \eta)$ in the presence of self-healing, so that the fracture stress $\sigma_F^{(SH)}$ becomes:

$$\sigma_F^{(SH)} = \frac{K_{IC}}{\sqrt{\pi a(1 - \eta)}} \quad (1)$$

This equation can be generalized in the case of nonlinear elastic materials, such as biological tissues like tendons or ligaments, for which the stress/strain constitutive equation can be expressed as $\sigma \propto \varepsilon^\kappa$, with κ constant ($\kappa > 1$ implies hyperelasticity while $\kappa < 1$ implies elastoplasticity).²³ Writing the equation in the form of the ratio between fracture stresses with and without self-healing, we get:

$$\frac{\sigma_F^{(SH)}}{\sigma_F} = \left[\frac{K_{IC}}{\sigma_F \sqrt{\pi a(1 - \eta)}} \right]^{2\alpha} = \frac{K_{IC}^{(SH)}}{\sigma_F \sqrt{\pi a}} \quad (2)$$

where $\alpha = \kappa/(\kappa + 1)$ and the modified fracture toughness for self-healing materials $K_{IC}^{(SH)}$ is:

$$K_{IC}^{(SH)} = \frac{\sigma_F^{(1-2\alpha)} (\pi a)^{\left(\frac{1}{2}-\alpha\right)} K_{IC}^{2\alpha}}{(1 - \eta)^\alpha} \quad (3)$$

which means that both the fracture stress and fracture toughness of a self-healing material are expected to scale as:

$$\sigma_F^{(SH)} \propto K_{IC}^{(SH)} \propto (1 - \eta)^{-\alpha} \quad (4)$$

with respect to the healing rate η .

As far as the fatigue life is concerned, one of the most widely used analytical laws is Paris’s law,²⁴ which describes the growth of a fatigue crack of length a as a function of the number of cycles N between two stress levels σ_{\min} and σ_{\max} in the case of a Griffith crack as $da/dN \propto (\Delta\sigma\sqrt{\pi a})^m$ where $\Delta\sigma = \sigma_{\max} - \sigma_{\min}$. Integrating this equation, we find that the number of cycles to failure N_C , arising when the crack length has reached its critical final value a_C , scales as $N_C \propto a^{(1-m/2)}$ for $a_C \gg a$ and plausible values of $m > 2$.^{25,26}

This scaling relation can once again be generalized for a self-healing material with the above hypothesis, so that:

$$N_C^{(SH)} \propto [a(1 - \eta)]^{(1-m/2)} \quad (5)$$

which can again be generalized for nonlinear elastic materials, giving:

$$N_C^{(SH)} \propto \left\{ [a(1 - \eta)]^{(1-m/2)} \right\}^{2\alpha} \propto (1 - \eta)^{\alpha(2-m)} \quad (6)$$

III. NUMERICAL HIERARCHICAL FIBRE BUNDLE MODEL FOR SELF-HEALING AND FATIGUE

As mentioned in Sec. I, tendons and ligaments display a fibrous structure, and several hierarchical levels can be identified,^{27,28} as shown in Fig. 1: from tissue level (~cm), to collagen fibers (~mm in length, ~μm in diameter), to collagen fibrils (~μm in length, ~100 nm in diameter), to collagen molecules (~300 nm in length, ~1 nm in diameter). Therefore, as in previous studies, we simulate their mechanical behavior using a HFBM,^{17,18} which extends the classical fiber-bundle model,¹⁵ adding hierarchical and self-healing effects. The HFBM procedure consists in discretizing a specimen in arrays of fibers arranged in series and parallel and assigning them statistically distributed fracture strengths, e.g., using a Weibull distribution.²⁹ Uniaxial loading is applied to the specimen and when fibers fail due to their strength having been exceeded, the load is redistributed among parallel fibers, e.g., according to an equal load sharing scheme.¹⁵ This allows the system to be analytically solvable at each iteration, i.e., the stresses acting on each fiber can be recalculated after each fracture event, as well as the mechanical properties of each section of the bundle, and the global stress-strain behavior. The model is implemented in a MATLAB code, which generates statistically distributed random fiber strength values from the chosen Weibull distributions for each fiber type, calculates the global stress-strain data for the selected loading protocol, and repeats the simulation with different random values over a sufficient number of iterations to derive statistically reliable average values.

For large systems, the code is run on a high-performance computing cluster at the Politecnico di Torino.³⁰

Hierarchical architectures can be modeled by using the simulation output of one particular hierarchical level (e.g., overall strength and stiffness) as the input for the statistically assigned mechanical properties at the next hierarchical level.¹⁶ Self-healing is included in this scheme by allowing fibers to be “regenerated” (healing event) as well as “eliminated” (fracture event) at a certain healing rate η , which is defined as:

$$\eta = \frac{N_{sh} - N_{s0}}{N_0 - N_{s0}}, \quad (7)$$

where N_0 is the initial number of fibers, and N_{s0} and N_{sh} are the numbers of surviving fibers with or without self-healing,¹⁸ respectively. If N_h and N_f are the numbers of healed and fractured fibers, respectively, in a given time interval, we have $N_{sh} = N_0 - N_f + N_h$ and $N_{s0} = N_0 - N_f$, so that:

$$\eta = \frac{N_h}{N_f}, \quad (8)$$

in accordance with the definition given in Sec. II. Finally, self-healing can take place at random locations in the specimen (distributed healing, in the case of microcracking) or at the location of the main advancing cracks (localized healing).

In the case of fatigue damage progression, modifications are necessary to the numerical model with respect to simulations involving simple monotonically increasing

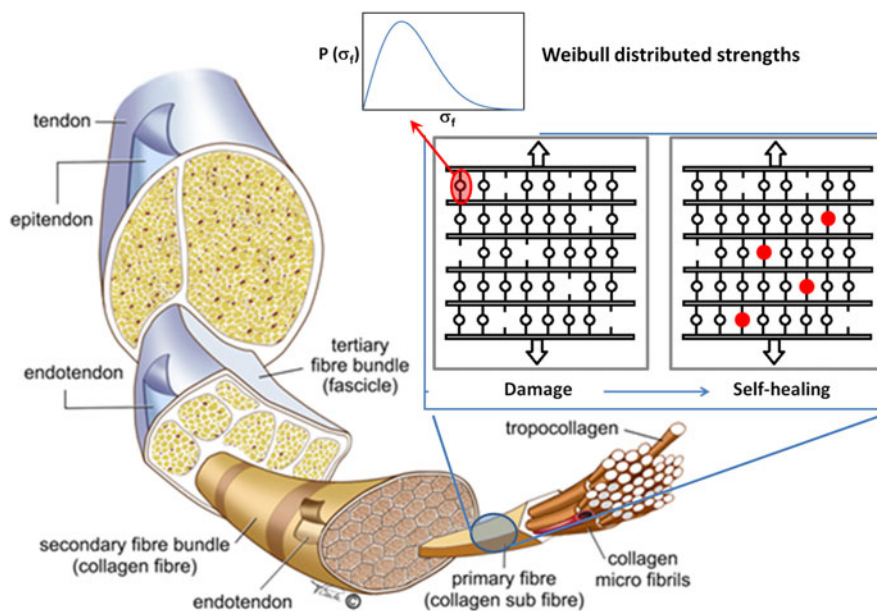


FIG. 1. Hierarchical fibrous structure of tendon, from tissue level to collagen fiber bundles, down to collagen fibrils (printed with permission of Vicky Earle and Karim Khan, and not to be reproduced further), and a schematic of the corresponding HFBM modelization including self-healing.

loads. This is due to the previously discussed Paris' law, which predicts a decrease of fatigue strength σ_C with increasing number of cycles:

$$\sigma_C \propto N_C^{-1/m}, \quad (9)$$

obtained by integrating Paris's law and taking $\sigma_{\min} = 0$, as in our case. The typical behavior is shown in Fig. 2 for $m = 3$ and various values of initial crack length a . Here, the fatigue strength is normalized with respect to nominal fracture strength.

Therefore, the failure criterion for the individual fibers in the HFBM is modified to include a stress threshold, whose initial value is assigned according to a Weibull distribution, which decreases with the number of fatigue cycles, according to Eq. (9).

When simulating biological materials, where the healed tissue is the same as the original one, the mechanical characteristics of the "healing agent" are the same as those of the "host material". This means that when healing occurs, fractured fibers in the bundle are replaced by fibers with statistically equivalent mechanical characteristics. To model tendons or ligaments, we use representative mechanical properties:¹⁹⁻²¹ Young's modulus $E = 650$ MPa, failure stress $\sigma_F = 80$ MPa, and failure strain $\epsilon_F = 15\%$. Weibull distributions with shape parameter $k = 2$ are used to obtain statistical dispersion around these mean values.

IV. NUMERICAL RESULTS AND ANALYTICAL COMPARISON

A. Fracture

We first wish to evaluate the validity of Eqs. (1) and (2) regarding the scaling of the strength of a self-healing

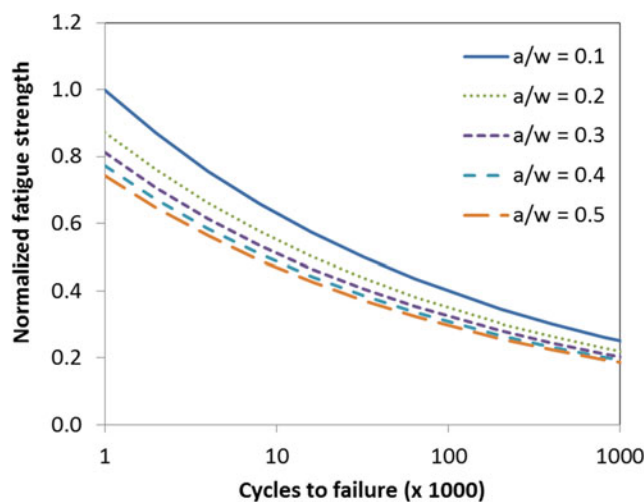


FIG. 2. Fatigue strength decrease with increasing number of cycles N_C , for various initial crack lengths a with respect to the specimen width w ($m = 3$). Fatigue strength is normalized with respect to nominal fracture strength.

material with its healing rate. To do this, we consider a specimen with a centrally placed pre-existing crack of length $2a$, loaded uniaxially in the direction of the fibers and perpendicular to the crack. To simulate such a pre-existing crack, an appropriate number of fibers in a central section of the fiber bundle are removed. The crack length a varies between 1/100th and 1/10th of the specimen width w , i.e., from 1 to 10% of the fibers are initially removed from the central section of the fiber bundle. Numerical simulations agree well with analytical values calculated with Eq. (2) in a wide range of parameters. As predicted by the theory, failure stress increases with respect to a and $(1 - \eta)$ according to the power law in Eq. (2). The results shown in Fig. 3, where failure stress is normalized with respect to nominal strength σ_0 without self-healing, refer to $a/w = 1/50$ and a best fit is obtained for $\alpha = 0.7$, corresponding to $\kappa = 2.33$, which is close to the hypothesized value of $\alpha = 0.5$ in the simulations. The discrepancy is due to the statistical nature of the simulations, in contrast with deterministic scaling laws. These simulations confirm the validity of this simple scaling and thus that, in the presence of self-healing, a Griffith's crack can be treated with an equivalent length of $a(1 - \eta)$. The obtained values for α (and κ) can be considered material constants, and will be used in the following sections.

B. Fatigue

The same type of sample considered in simulations in Sec. IV. A is subsequently considered under cyclic fatigue loading. Various types of imposed displacement are adopted, including "saw tooth"-like functions, where the strain is increased linearly up to a maximum value, then decreased to zero, and then ramped-up again cyclically, or "rectified sine"-like functions, where the imposed strain varies with the absolute value of a sine function.

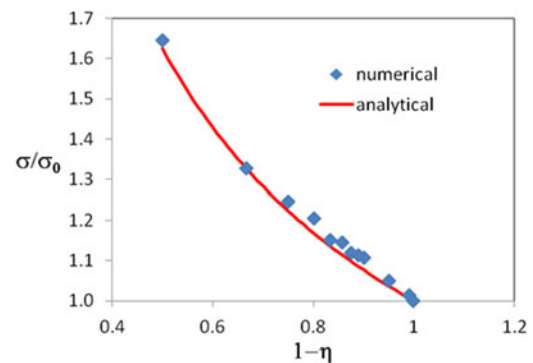


FIG. 3. Comparison between numerical simulations and analytical values based on Eq. (2) (Griffith's law generalized to include self-healing) for the failure stress σ of a centrally cracked specimen as a function of its healing rate. Failure stress is normalized with respect to nominal strength σ_0 without self-healing, and best fit is obtained for $\alpha = 0.7$.

An example of the obtained behavior, in the absence of self-healing, is shown in Fig. 4(a) for a saw tooth cyclic strain profile. Both stresses and strains are normalized with respect to their maximum amplitude ϵ_0 and σ_0 in

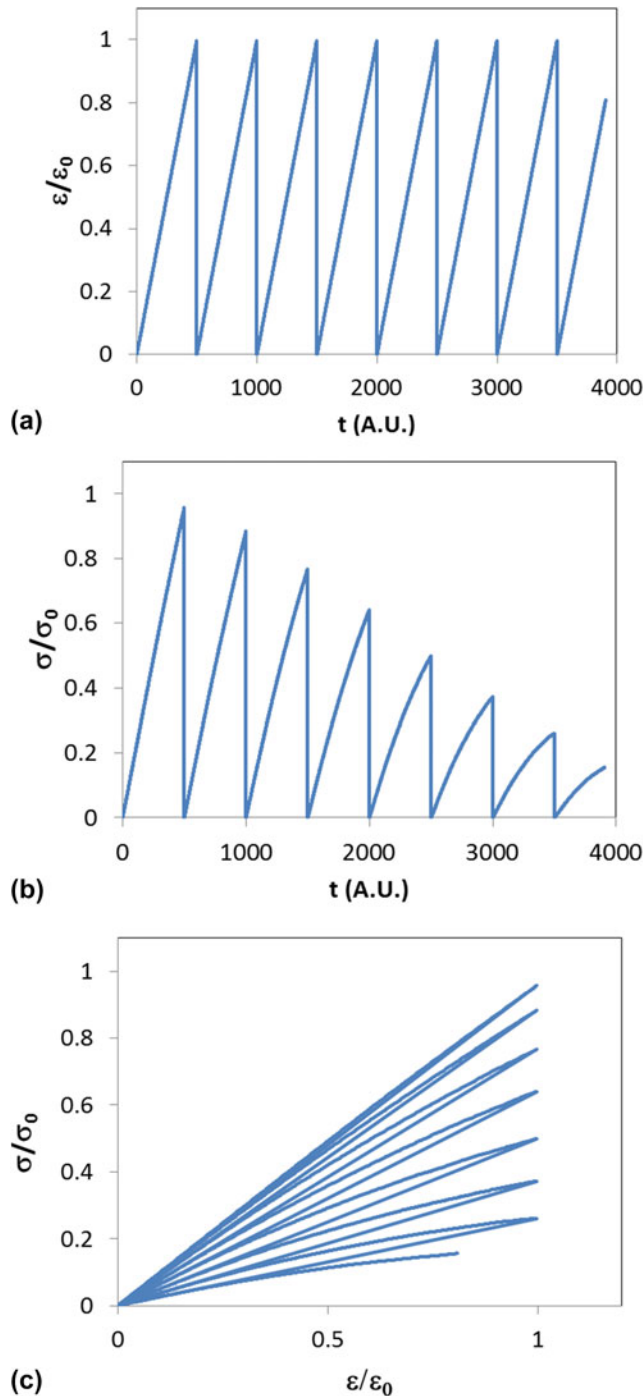


FIG. 4. Example of a simulation of fatigue cycling and corresponding stress–strain behavior: (a) Cyclic “saw tooth” imposed strain; (b) Corresponding stress evolution; and (c) Resulting stress–strain curves with increasing fatigue damage. Time scales are given in arbitrary units (A.U.) since no explicit time dependence is included in the model.

the fatigue cycles. Here, the maximum imposed strain value is chosen near the failure strain of the material (80% of the value), so that considerable damage progression is achieved over a limited number of cycles. This is shown in Fig. 4(b), where the stress amplitude is seen to drop considerably over a few fatigue cycles, due to specimen damage, and in Fig. 4(c) where the specimen stress–strain curves display increasing material softening as damage progresses, up to final specimen failure.

The effect of self-healing on the simulated behavior can be visualized in Fig. 5 for $\eta = 0.1$ in a distributed healing configuration: The stress softening effect due to progressive damage is reduced considerably [Fig. 5(a)], in particular, for early stages of damage, and the fatigue lifetime is increased by approximately 34%. At the same time, the dissipated energy during fatigue cycling, calculated as the area included between the ascending and descending stress–strain curves in a single cycle, is reduced considerably in the presence of self-healing [approximately 47% per cycle, Fig. 5(b)]. Clearly, this calculation does not account for the energy necessary

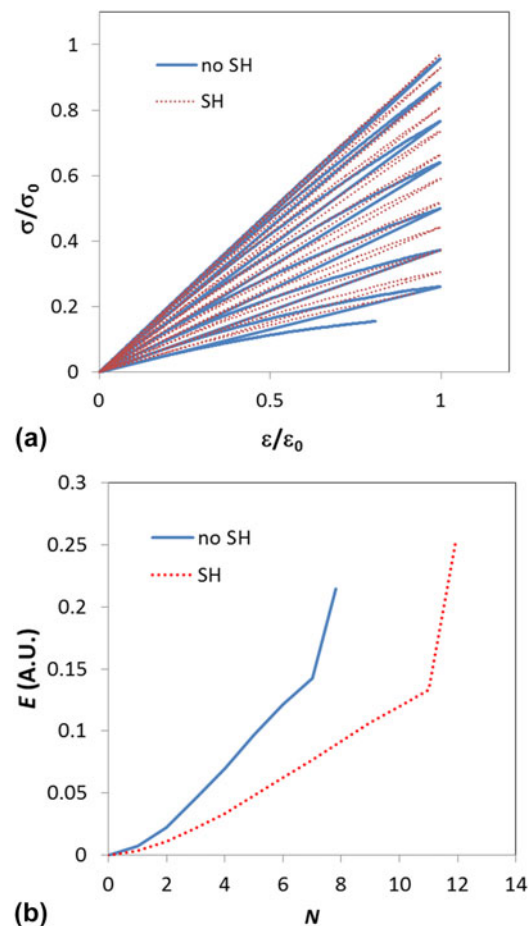


FIG. 5. Example of a simulation of fatigue cycling with (“SH”) or without (“no SH”) self-healing: (a) stress–strain curves. A healing rate of $\eta = 0.1$ is chosen in a distributed healing configuration. (b) Normalized dissipated energy.

to provide self-healing itself. At specimen failure, the self-healing specimen dissipates a greater amount of total energy, since it fails at a higher stress value with respect to the non-self-healing one.

The effectiveness of self-healing is greatly dependent on the mechanical properties of the “healing agent”, i.e., in biological materials, the tissue that replaces the damaged material. This can be seen by varying the strength σ_{FSH} of the new fibers that replace damaged ones in simulations, with respect to that of the original ones σ_{F0} . Three ratios between the two strengths are considered in Fig. 6: $\sigma_{F0}/\sigma_{FSH} = 100, 10, 1$. Simulations show a nonlinear increase in the fatigue life N_C of the considered specimen with increasing healing rate for all three cases, but a markedly more significant maximum increase (42%) in the case of $\sigma_{FSH} = \sigma_{F0}$, although a significant 31% maximum increase is obtained for a poor healing agent having only $\sigma_{F0}/\sigma_{FSH} = 100$. This suggests the robustness of the strategy emerged in nature during the Evolution process: even a small healing rate can result in a strong toughening of the material.

These calculations can be used to interpret data in the literature regarding in vitro tests on biological tissue, where mechanical properties are derived without the effect of self-healing. For example, Schechtman and Bader¹⁹ performed mechanical tests on human extensor digitorum longus (EDL) tendons, which are involved in joint movement at the foot and ankle. In particular, they derived the fatigue life for 90 specimens as a function of the maximum fatigue stress, expressed as a percentage of the experimentally measured tendon fracture stress. These data are reported in Fig. 7 (“no SH” fitted with our model for $\eta = 0$), together with the corresponding fatigue life extrapolations for different values of healing rate η , which in this case would also be dependent on

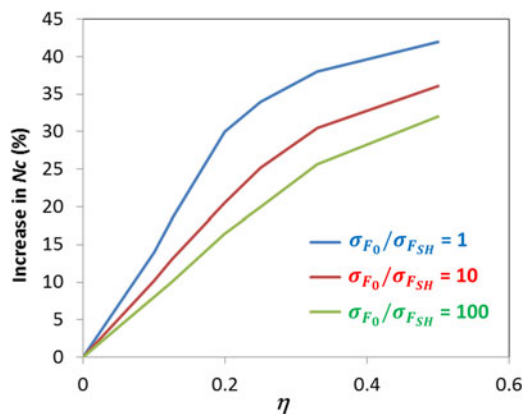


FIG. 6. Evaluation of the increase in fatigue life (N_C) as a function of healing rate η for varying “healing agent” mechanical strength σ_{FSH} with respect to the original material strength σ_{F0} . The small differences in fatigue life imposed by huge variations of healing agent strengths suggest the self-healing robustness of the strategy emerged in nature during evolution.

fatigue cycle speed. For example, in the case of $\eta = 0.2$, when cycling at 20% of the failure stress, one would obtain an increase in N_C of approximately 30%. In practical terms, for an athlete, this would mean that in the absence of tendon self-healing, and assuming an active sporting life of up to 40 years, tendon overuse problems or fracture would occur up to ten years earlier for equivalent loading.

Simulations also allow us to verify the validity of the generalized Paris’ law hypothesized in Sec. II. The results are shown in Fig. 8: the scaling of fatigue life N_C of self-healing specimens with respect to $(1 - \eta)$ is calculated numerically and analytically, using Eq. (6), for various initial crack lengths a , normalized with respect to the specimen width w . A saw tooth loading function is used and the fatigue stress level is chosen to be approximately 5% of the fracture strength of fibers, so as to obtain a significant number of cycles to failure ($>10,000$). Numerical results show a power-law decrease in the average fatigue life with $(1 - \eta)$, consistent with the theory. These can be fitted with power-law functions, as shown in the figure. Contrary to uniaxial tension numerical simulations, where localized healing proved to be considerably more effective than distributed healing in increasing fracture strength, in the case of the present fatigue simulations, the difference between results for the fatigue life in the two cases is negligible, again suggesting the robustness of the self-healing.

To fully verify Eq. (6), the N_C results are plotted versus $a(1 - \eta)$. Figure 9 shows data for distributed healing. The numerical data can be adequately fitted using a power-law $y = a \times x^b$, with a resulting exponent of $b = -0.698$. Comparing this to Eq. (6) and using the previously derived value of $\alpha = 0.7$, we obtain a Paris exponent of $m = 2.5$, which is smaller than values found for other collagen-based materials such as bone (which can have lower values of $m = 4$),³¹ but is com-

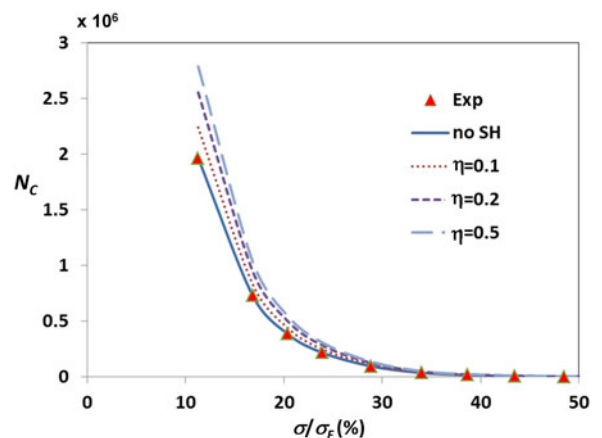


FIG. 7. Fatigue life (N_C) as a function of maximal stress amplitude divided by strength for various η values. Experimental data (“Exp”) fitted by the $\eta = 0$ curve (“no SH”) are taken from Ref. 19.

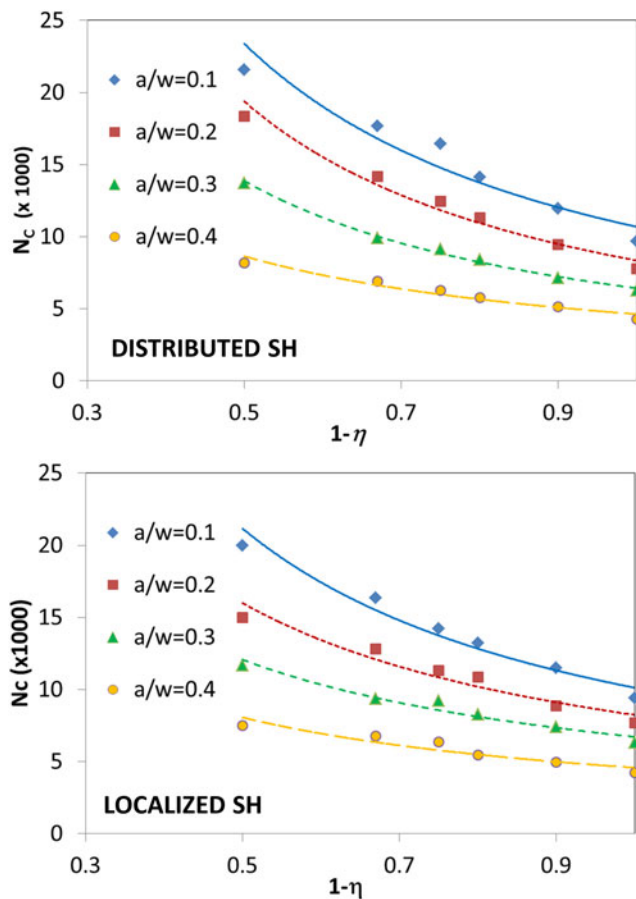


FIG. 8. Dependence of numerically calculated fatigue life as a function of $(1 - \eta)$ for distributed (above) or localized (below) healing. Data are interpolated with the derived power law scaling.

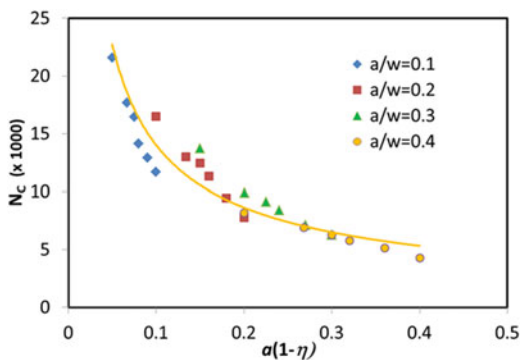


FIG. 9. Numerical validation of the generalized Paris' law for self-healing materials: comparison between numerically and analytically calculated fatigue life as a function of $a(1 - \eta)$.

parable to other biological materials.³² More importantly, the output value of $m = 2.5$, although close to the input value of $m = 3$ used in Eq. (9), also confirms that our code is able to predict scaling of the Paris's exponent. More importantly, we also notice that this m value is consistent with that used in simulations to describe the fatigue stress decrease according to Eq. (9).

V. CONCLUSIONS

We have developed and modified our previous code, the HFBM, to simulate fatigue damage evolution in self-healing soft nanomaterials. The model is essentially dependent on a single parameter, the material healing rate, which defines the degree of material reparation versus material damage. How the healing occurs, whether at the location of the main advancing crack, or at random damaged locations in the specimen, does not seem to appear to influence significantly the effectiveness of the reparation process. The results show that the fatigue life can be considerably improved with respect to non-self-healing specimens, with increases of up to 40% for healing rates close to 0.5. The mechanical properties of the healing agent are also shown to play a significant role: biological materials, even when the healing agent does not have the same high-level properties of the original material, have a potential advantage over non-self-healing materials suggesting that also artificial self-healing materials, where healing agents often have reduced mechanical properties, could represent interesting bioinspired solutions. Finally, numerical simulations are used to confirm simple scalings that have been introduced for the expressions of fracture or fatigue in the case of self-healing materials.

On the one hand, this study highlights the robustness of the self-healing strategy adopted in nature as a consequence of evolution. On the other hand, the present numerical approach and modified analytical expressions for Paris' law provide the possibility of improving fatigue life predictions in medicine, e.g., the fatigue life of in vivo tendons of sportsmen. Of course, further studies are needed to verify the applicability of Paris' law, which was first developed for materials such as metals, in the field of soft materials such as tendons. However, in support of this approach, a number of studies are present in the literature for collagen-based materials (see Ref. 33 and references therein), particularly in the case of bone, showing that Paris' law is applicable. This, together with the particularly robust and wide-ranging applicability of Paris' law for many materials, leads to the assumption that it should be appropriate for tendons and ligaments.

In future, the influence of hierarchy on fatigue performance will be studied in depth, and this model will also be used to develop strategies for the simultaneous optimization of multiple material properties, such as strength, toughness, and fatigue life, with the objective of better understanding biological materials and thus helping in finding ultimate solutions in sport medicine, as well as in the design of novel bioinspired materials.

ACKNOWLEDGEMENTS

NMP acknowledges support from the European Research Council, ERC Ideas Starting Grant No. 279985 "BIHSNAM", from ERC Proof of Concept

Grant No. 619448 “REPLICA2” and No. 632277 “KNOTOUGH”, from the Graphene FET Flagship (“Graphene-Based Revolutions in ICT And Beyond”-Grant agreement No. 604391), and from the Autonomous Province of Trento (Graphene PAT WP10, code 81017). FB acknowledges support from BIHSNAM. The authors also acknowledge support for computational resources from Politecnico di Torino’s DAUIN High Performance Computing Initiative (www.dauin-hpc.polito.it).

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