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A topological weakening and softening map as simplified tool to assess the performances recovery of hybridized natural fiber reinforced composites subjected to alternate salt-fog/dry cycle

L. Calabrese [a,*], V. Fiore [b], A. Valenza [b], E. Proverbio [a]

[a] Department of Engineering, University of Messina, Contrada Di Dio (Sant'Agata), 98166, Messina, Italy
[b] Department of Engineering, University of Palermo, Viale delle Scienze, Edificio 6, 90128, Palermo, Italy

A B S T R A C T

While receiving a growing attention in recent years, natural fibers cannot completely replace synthetic fibers as composite reinforcement for structural applications due to both their low durability in wet or humid environments and their limited and not homogenous overall performance. In this context, the purpose of this paper is to assess the impact of a humid/dry cycle on the mechanical stability of epoxy-based laminates reinforced with flax and glass fibers by using a topological weakening and softening map as simplified tool. The objective is, preliminarily, to evaluate the influence of glass fiber hybridization on the properties recovery of flax fiber reinforced composites subjected to alternate salt-fog/dry cycle. All laminates studied were subjected to salt spray for 15 or 30 days, and then stored in a dry controlled environment (50% relative humidity and 22 °C) for up to 21 days. The results evidenced that, compared to flax fiber reinforced composites, the glass hybridization of flax composite significantly reduce the mechanical performances degradation over time during the humid stage (about 28.0% better than flax one in stiffness). Furthermore, the mechanical performance recovery is promoted during the dry stage. A simplified topological map was lastly developed to graphically assess the decline and recovery of composites' performances during the humid/dry cycle, amplifying the application and design effects of this approach.

1. Introduction

Due to their desirable mechanical properties, lightweight, and resistance to corrosion, fiber-reinforced composites have received relevant attention in recent years. In this concern, natural fiber reinforced composites (NFRC) have gained an increasing research interest due to their potential environmental benefits [1–4]. However, natural fibers, such as flax one, have some limitations when it comes to their durability in harsh environmental conditions.

Flax fiber is a natural fiber that has some advantages over synthetic fibers such as low cost, low density, and high specific mechanical properties. However, its main limitation is its poor resistance to humidity and UV radiation. When exposed to these severe environmental conditions, the mechanical properties of flax fiber composites tend to degrade over time, leading to a reduction in their overall performance [5,6].

Flax fiber is a natural fiber that, compared to synthetic ones, has several advantages, such as low cost, low density, and high specific mechanical properties. However, a relevant drawback that limits its use in marine outdoor structural applications is the scarce resistance to severe environmental conditions (e.g. UV light, wet or humid environments). Thus, the mechanical performances of NFRC tend progressively to degrade over time when exposed in these conditions [6,7].

To overcome this issue, several research activities were addressed toward the assessment of the hybridization of flax fibers with other synthetic fibers having higher durability, such as glass fibers considering its high strength, stiffness, and resistance to severe wet and humid conditions [8]. In particular, the hybridization of flax fibers with glass fibers involves a synergistic combination of the two different fibers in order to design a multi-fabric composite material able to maximize the beneficial contributes of both fibers.

When exposed to humidity, composite laminates suffer the activation and propagation of several competing degradation mechanisms such as hydrolysis, swelling, and fiber/matrix interface degradation that support an accelerated aging over time [9–11]. The tailoring of a specific stacking sequence of hybridized glass-natural fiber reinforced composites can be identified as a key factor to prevent or delay the composite material degradation thus improving its durability in wet conditions.

In this perspective, the choice of natural and synthetic fibers with peculiar capabilities, as well as the matrix properties and the manufacturing process are suitable approaches to optimize the durability performances of the hybrid composite laminate [12–14].

A possible strategy, widely investigated in the literature is to use a polymeric matrices characterized by a relevant resistance to water or

* Corresponding author.
E-mail address: lcalabrese@unime.it (L. Calabrese).

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moisture absorption, such as epoxies or vinyl ester ones [15,16]. This can help to prevent the degradation of the matrix and consequently strongly limit the triggering of degradation phenomena of the compound over time.

Another approach that achieved promising results is to improve durability in wet or humid conditions by using outer glass fiber reinforced layers in NFRCs. This can help to protect the natural fibers in the inner layers of the composite from water induced damage.

In such a context, a lot of paper are available in the literature about the effectiveness of hybridization of lignocellulosic fibers with stronger and more aging resistant synthetic ones such as glass [17] carbon [18] and Kevlar [19] as well as mineral fibers, such as basalt [20–22].

Another recent study by Fiore et al. [23] investigated the effect of the hybridization with external glass woven fabric-reinforced laminae on pinned bearing strength of flax fiber reinforced composites. The results showed that for this stacking sequence, the processes of plasticization and performances decay are strongly hindered, with beneficial effects on the mechanical stability at varying aging time in salt-fog environment.

However, one aspect that has not been sufficiently addressed is understanding how the performances degradation that occur in composite laminates, whether hybridized or not, can be recovered in a reversible manner when the aging conditions in humid environments are alternated or interrupted [24,25].

In such a context, our efforts were recently addressed on the evaluation of the aging behaviour of flax [26,27], glass [28], and hybrid flax–glass [29] fiber reinforced epoxy based composites under alternated salt-fog exposition and dry stages, typical conditions of marine applications.

In particular, when the composite is left to dry after the wetting or humid period, there can be a progressive reduction in the plasticization induced by water absorption, resulting in a consequent recovery of strength and stiffness [29]. Similarly, shrinkage, interfacial debonding and permanent weakening of the material may also occur [30]. This degradation can affect the residual strength, stiffness as well as other mechanical properties of the composite, which are crucial in determining the material's performance in various applications.

Considering that natural fiber-based composite laminates are susceptible to degradation when exposed to aggressive outdoor environments, it is essential to have suitable analysis systems that support the design and durability prediction of these materials in such environments.

The analysis systems should allow us to predict the mechanical properties of composite laminates under different environments, thus helping in the design of these materials that can withstand harsh conditions. It should also be able to predict the degradation rate of the composite laminates under real environmental stresses, giving a support to define the service life of the composite laminates.

Therefore, understanding how much composites can recover their mechanical properties after being subjected to alternate humid/dry cycling is critical to assess their durability and reliability in practical applications, such as outdoor marine environments. This knowledge can aid in designing and tailoring composites with improved durability and can help to identify optimal conditions for maintaining and repairing existing composites that have been exposed to humid/dry outdoor cycles.

In this context, the main aim of the paper is to assess the influence of glass fiber hybridization on the properties recovery of flax fiber reinforced composites subjected to alternate salt-fog/dry cycle, such as outdoor marine environments, by using a topological weakening and softening map as simplified tool. All laminates studied were subjected to salt spray for 15 or 30 days, and then stored in a dry controlled environment (50% R.H. and 22 °C) for up to 21 days. Water uptake, three-point flexural test and fracture morphology results over humid/dry time were integrated to identify reversible and permanent degradation of the mechanical performances. In particular, the effect of the stacking sequence on the mechanical behavior under varying environmental conditions was studied. Finally, a simplified topological map was developed in order to assess graphically the performance decline and recovery during humid/dry cycle.

2. Experimental part

2.1. Material and methods

30 × 30 cm^2 square laminates were manufactured for each investigated staking sequence by means of vacuum infusion technique through a two-stage vacuum pump model VE 235 D (Eurovacuum, Reeuwijk, The Netherlands). Each laminate was cured at room temperature for 24 h and post-cured at 50 °C for 15 h, according to the technical datasheet of the commercial epoxy resin (SX8 EVO by Mates Italiana s.r.l., Milan, Italy) used as matrix.

A 2 × 2 twill weave woven flax fabric (318 g/m^2 areal weight) supplied by Lineo (Saint Martin du Tilleul, France), and a plain weave woven glass fabric (200 g/m^2) supplied by Mike Compositi (Milan, Italy) were used as reinforcement.

Table 1 summarizes the details of the manufactured laminates. Laminates are coded with suffix HC, GC and FC for hybrid, glass and flax composites, respectively.

All stacking sequences have been defined in order to keep constant the composites' thickness (i.e., equal to about 3.5 mm). This was done in order to ensure a more effective comparison of the adsorption/desorption phenomena and related mechanical properties.

2.2. Salt-fog/dry aging

All laminates were preliminary exposed to a salt-fog/dry aging cycle. This aging set-up was used to test the material durability in alternate aging conditions. The cycle involves exposing the materials to a salt spray fog and then drying them in a controlled environment.

The salt-fog spray test is performed according to ASTM B117 standard. In particular, all composites were placed inside a climatic chamber SC/KWT 450 by Weiss (Buchen, Germany) and exposed to a continuous spray of salt solution (5 wt% sodium chloride) at 35 °C ± 1 °C for 15 or 30 days, in order to simulate the aging induced by a real marine outdoor environment. It is worth noting that all composite panels were aged whole in the salt spray chamber to limit the diffusion of water across the edges, hence imposing only the water diffusion transversely to the plane of the fiber fabrics.

At the conclusion of the salt-fog exposition, each panel was cut with a diamond blade saw to obtain prismatic samples (13 mm × 64 mm) for the three-point flexural characterization. In particular, five samples were tested immediately for each stacking sequence and salt-fog exposure time (i.e., 15 and 30 days) to determine how the humid stage affected the mechanical behavior of the composite laminates.

Further samples (i.e., thirty-five for each composite) are moved and stored in a climate-controlled room. This allows the materials to dry out, simulating the effects of cyclic exposure to alternate salt water and drying cycle. The dry stage is carried out setting the relative humidity and temperature at 50% ± 10% and 23 °C ± 2 °C, according to ISO 291:2008 standard. For each stacking sequence, five samples were periodically removed and tested at varying dry times (0.5, 1, 2, 3, 7, 11, and 21 days). Although the cut edges will facilitate faster drying and shorter recovery times, the decision to cut the wet samples prior to drying was made in order to optimize the various dry batches for the

Table 1
Details of the composite laminates.

CODE	Stacking sequence*	Thickness [mm]
HC	$[G_2/F_2]_s$	3.56 ± 0.04
GC	$[G_{18}]$	3.59 ± 0.08
FC	$[F_5]$	3.35 ± 0.02

experimental campaign. A schematization of the panel manufacturing and alternating salt spray humid/dry aging cycle is reported in Fig. 1.

All the investigated batches were codified by adding to the prefix indicating the staking sequence(i.e., FC-, HC-, or GC-), a suffix (i.e., HhDd) representing the time duration in days of humid (h) and dry (d) stages, respectively. For instance, the HC-H30D7 code refers to hybrid samples exposed to salt-fog chamber for 30 days and then dried for 7 days whereas the HC-H0D0 code is referred to hybrid unaged samples (i.e., reference).

2.3. Water uptake

The water uptake progression of hybrid composites was assessed throughout humid and dry stages, in accordance with ASTM D570 standard [31]. In the humid stage, two square laminates (100 mm × 100 mm) were intermittently removed from the salt-fog chamber, wiped down with a dry, clean cloth, and weighed by using a precision balance model AX 224 by Sartorius (Gottinga, Germany). In the dry stage, the weight of both H15 and 30 batches (aged in salt-fog chamber for 15 and 30 days, respectively) was observed to determine the capability of the hybrid laminates to regain mass under regulated environmental conditions. The water uptake (WU) exhibited by all laminates was calculated at different time intervals throughout the humid/dry cycle, utilizing the subsequent formula:

$$\boldsymbol{WU}\ [\%] = \mathbf{100} \bullet \frac{\boldsymbol{M_{ti}} - \boldsymbol{M_U}}{\boldsymbol{M_U}} \qquad \text{Eq. 1}$$

where M_U and M_{TI} are the weight of dry (i.e., unaged) and aged samples (i.e. exposed for ti time to salt-fog), respectively.

Furthermore, to assess the water absorption and desorption characteristics of the GFRP composite, the diffusion coefficients were evaluated separately for the humid (i.e., absorption) and dry (i.e., desorption) stages. Fick's theory was employed to model the moisture uptake phenomenon and determine the moisture diffusion coefficients [32]. According to the Fick's second law of diffusion, the theoretical mass alteration (Mt) can be computed as follows [33]:

$$M_t = \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-(2n+1)^2\pi^2 \frac{D_{ads}t}{h^2}\right)\right] M_\infty \qquad \text{Eq. 2}$$

Where D_{ads} is the diffusion coefficient in adsorption, M_∞ is the mass gain (water uptake) at saturation, h is the sample thickness, and t is the sorption time. The desorption process was investigated using the same strategy. As a result, the loss of moisture during the dry stage can be analogously defined as [33]:

$$M_t - M_\infty = \left[\sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-(2n+1)^2\pi^2 \frac{D_{des}t}{h^2}\right)\right](M_0 - M_\infty) \qquad \text{Eq. 3}$$

Where D_{des} is the diffusion coefficient in desorption. The adsorption and desorption diffusion coefficients, D_{ads} and D_{des}, were computed by minimizing the sum of the squares of the deviations of theoretical values from the experimental ones.

2.4. Density and void content

The apparent density (ρ_a) of both unaged and aged samples were determined using a helium pycnometer (Ultrapyc 5000 foam by Anton Paar, Graz, Austria) and weight measurement at the end of the humid and dry stages. The same analytical balance employed for water uptake monitoring was utilized. The measurements were conducted ten times for each sample. Besides, the theoretical density (ρ_{th}) of the samples was calculated, according to the mixture rule, by:

$$\rho_{th} = \frac{1}{\sum_{i=1}^{n} W_i/\rho_i} \qquad \text{Eq. 4}$$

Where, W_i and ρ_i are the weight fraction and density, respectively, referred to i-th composite constituent (i.e., matrix, glass and flax fibers). Furthermore, the volume fraction of voids (V_V) was calculated, according to ASTM D2734 standard [34], by:

$$V_V = \frac{\rho_{th} - \rho_a}{\rho_{th}} \qquad \text{Eq. 5}$$

2.5. Three-point bending tests

A universal testing machine (UTM) model Z005 with a 5 kN load cell (Zwick-Roell, Ulm, Germany) was used to mechanically test all composite batches for each humid and dry combination (five composite samples with dimensions 13 mm × 64 mm for each condition).

Following the ASTM D790 standard [35], the crosshead speed and support span were set to 54 mm and 1.4 mm/min, respectively, to carry out the three-point bending tests. This kind of test was chosen in order to achieve the most effective contribute of the glass fiber reinforced layers, stacked in the outer laminae in the hybrid composites. This stacking sequence has been shown experimentally to be suitable for improving the aging resistance of hybrid synthetic-natural fiber reinforced

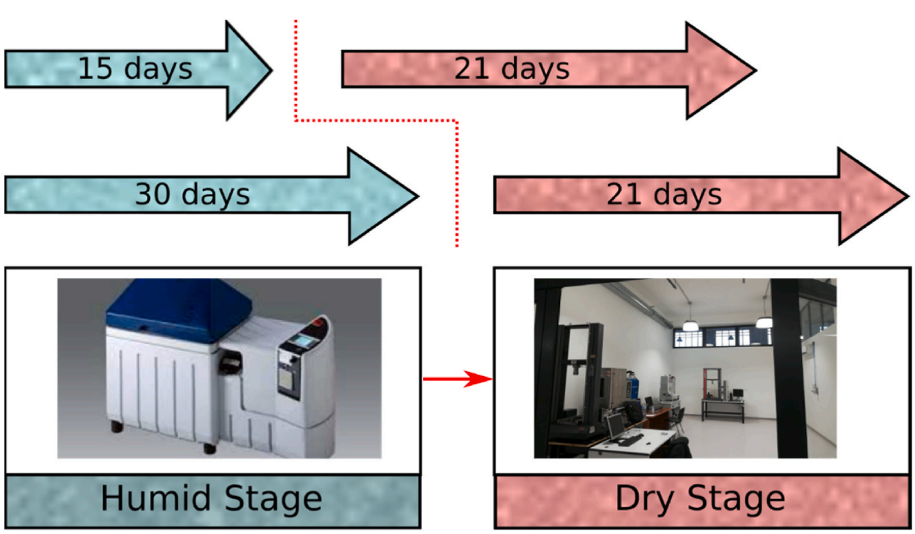

Fig. 1. Schematization of the humid/dry aging stages.

composites [20,36].

3. Results and discussion

3.1. Water sorption and desorption during humid/dry cycle

Fig. 2 shows the water uptake for all composite batches at increasing the aging time (i.e., samples exposed to salt-fog for15 days and 30 days in Fig. 2a and b, respectively).

The results show that as the duration of exposure to a humid environment increased, the weight of all samples progressively increased. This effect is particularly noticeable in the flax laminates and became less significant as the glass fiber content in the laminate stacking sequence increased. In other words, the increase in weight was less pronounced in samples with a higher glass fiber content.

In particular, 15 days of exposure in a salt spray chamber are enough to impose a 7.9% increase in weight for the natural fiber laminate, about 10 times higher than that of glass one. This finding is in agreement with the results achieved by Assarar et al. [37], who compared flax and glass fiber reinforced composites evidencing that the water absorption of natural composite is about 12 times higher than synthetic one. Thanks to the hybridization arranging glass fibers externally to a flax fiber core, it

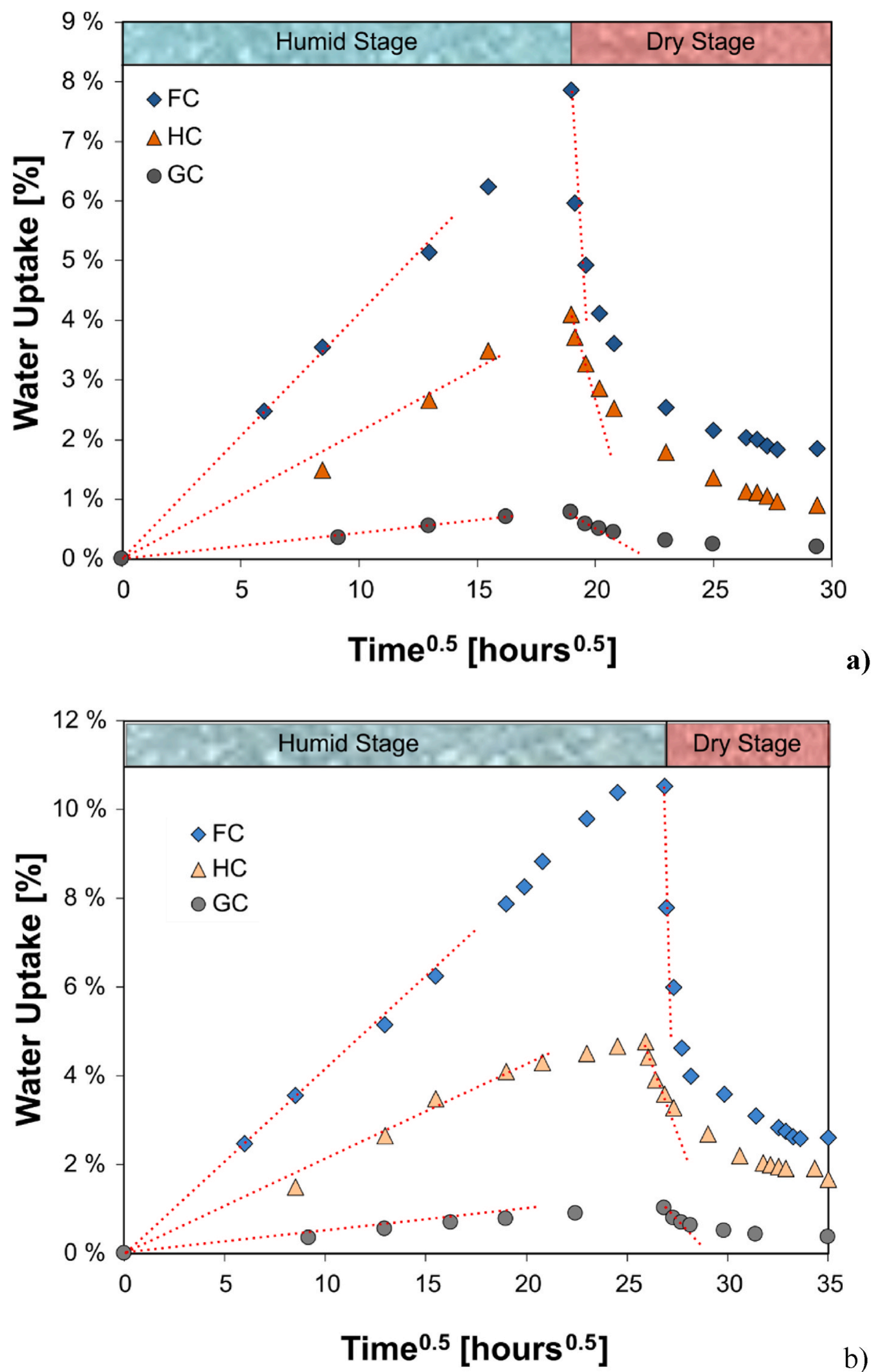

Fig. 2. Water uptake trends for FC, GC and HC samples at increasing the aging time: samples aged (a) 15 days and (b) 30 days in salt-fog chamber.

is possible to notice an improvement in water absorption of HC batch during the humid stage, compared to GC one, obtaining a maximum absorption of about 4%, intermediate between the full-flax and full-glass laminates. These results suggest that the moisture absorption rate of laminates is influenced by the type and amount of fibers used in the stacking sequence.

By evaluating the water uptake trend at longer salt-fog exposition (i.e., 30 days), it is possible to notice a progressive stabilization of the curve evolving toward an asymptotic equilibrium value. This trend is mainly identifiable for flax fiber-based composite laminates (i.e., FC and HC batches). The maximum water uptake values, observed at 30 days of exposition in salt-fog environment, were equal to 10.5%, 4.8%, and 1.0%, for FC, HC and GC composites, respectively.

This behavior can be related to the microstructure features of the fibers, that affects their ability to absorb water, or lack thereof.

Flax fibers, are known for their high hydrophilic behavior and relevant water absorption capacity [27]. This behavior is attributed to the porous structure of lignocellulosic fibers, featuring dense shells, a central light core (lumen), and numerous small free spaces that act as preferential water absorption containers [38–40].

In contrast, glass fibers are hydrophobic thus showing very low water absorption [41,42]. This behavior stems from the amorphous solid nature of the glass fibers, hindering water molecule penetration. Additionally, the surface of glass fibers is smooth and non-porous, providing little opportunity for water to adhere or be absorbed.

During drying, the water uptake trend in the composite laminates undergoes an inversion. Indeed, the water uptake decreases as the absorbed water evaporates progressively. This trend is more noticeable with shorter drying times, and the slope of the curve decreases as drying time increases, eventually stabilizing. This suggests reversible release of water absorbed in the humid stage during the following dry stage. However, the residual weight gain after extended drying times indicates that some local degradation processes occurred during the humid stage [28].

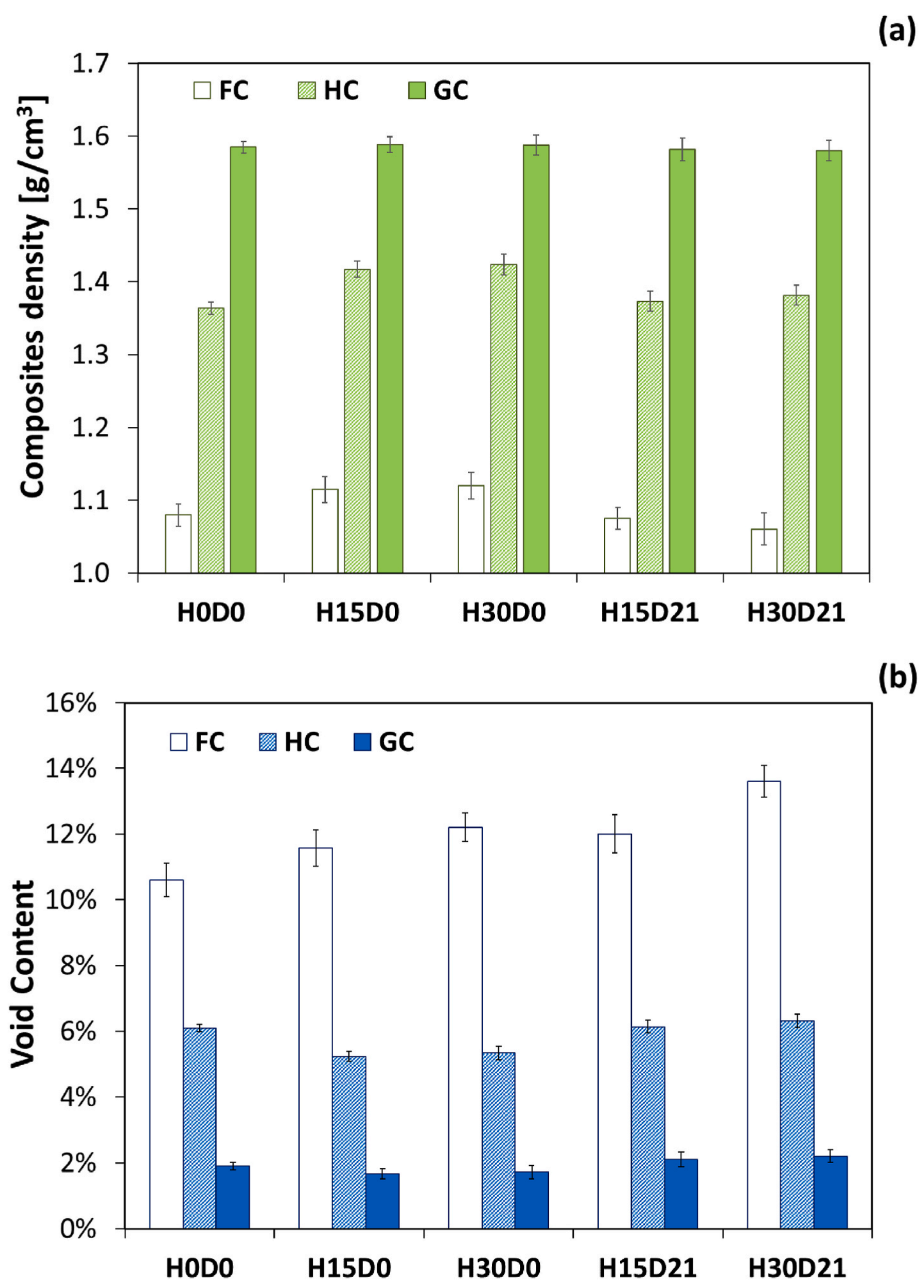

Fig. 3. a) Density and b) void content values for all composite batches for different humid and dry conditions.

Fig. 3a and b show the composite's bulk density and void content values at various humid and dry conditions.

The stacking sequence of composites clearly influences their bulk density, which increases progressively with increasing glass fibers content. The unaged H0D0 batches show increases in bulk density from 1.080 g/cm^3 to 1.364 g/cm^3 and to 1.585 g/cm^3 for flax, hybrid and glass laminates, respectively. Besides, by evaluating the density values at varying aging conditions, it is identifiable that the exposure to salt-fog increases the density of the composites, with the effect being more evident for the flax laminate, for which an increase of 3.7% in the density is observed after 30 days of salt-fog exposition (i.e., FC-H30D0 batch)

This can be justified based on the hydrophilic nature of the flax fibers coupled to the low fiber/matrix interfacial adhesion of the natural fiber reinforced composite [43].

These hypotheses are also provided by evaluating the evolution of the void content for all laminates during the humid/dry cycle. In fact, during the humid stage, there is a reduction in the volume of voids that is greater the higher the increase in density, indicating that the absorbed water penetrates the structure, thus limiting the voids [44,45].

During the dry stage, the density of all laminates decreases and void content increases, probably due to absorbed water that dry out thus increasing the number of residual voids or cracks in the composite bulk. For the H30D21 laminates (i.e., exposed for 30 days to salt-fog and then dried for 21 days), FC, HC and GC samples exhibited density values equal to 1.060 g/cm^3, 1.381 g/cm^3 and 1.580 g/cm^3 respectively. Hence, a large deviation in density from the unaged status was observed, suggesting that it has undergone the activation of larger degradation phenomena during aging compared to the other laminates.

In order to better evaluate how the water molecules interact with the composite laminates during the humid and dry stages of the aging cycle, the diffusion coefficient values related to the sorption and desorption processes were evaluated, according to Eq. (2). The results are summarized in Fig. 4.

By comparing the composite laminates with different stacking sequence, it can be noted that the flax fiber reinforced composite is characterized by the lowest diffusion coefficient in the sorption process (D_{sor}). This behavior is attributable to the different interaction of natural and synthetic fibers with water molecules. In particular, flax fiber has a prominent hydrophilic nature which exalts the affinity with the water, thus triggering the water/composite surface interaction and the diffusion processes towards the composite bulk. This latter process is kinetically slower mechanism which imply longer absorption saturation times. Conversely, glass fiber offers greater shielding action against the absorption and diffusion of water, involving mainly surface interaction phenomena between the composite and the water molecules absorbed

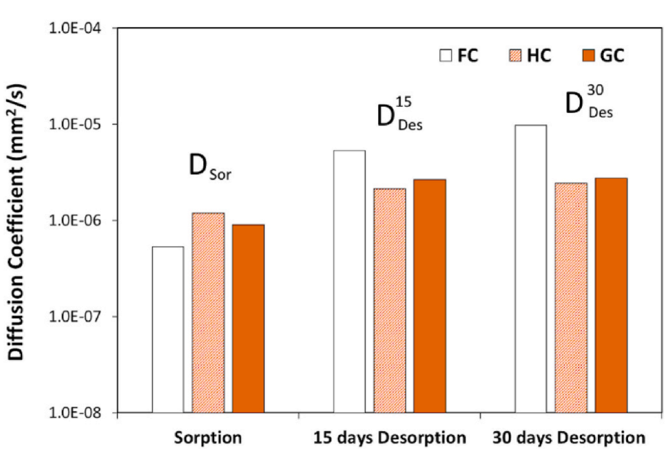

Fig. 4. Diffusion coefficient values for all composite batches during sorption and desorption steps.

[46]. In this case, the higher diffusion coefficient values involve rapid phenomena from the kinetic point of view, i.e., characterized by low absorption saturation times). The values found for the glass and hybrid laminates are comparable (the error bars are partially overlapped for these batches). The larger dispersion of D_{sor} value in the hybrid laminate could be due to the presence of local defects, interfacial or interlaminar adhesion issues, which amplify the structural heterogeneity intrinsically present in this laminate. The output is a greater dispersion of the data as evidenced in Fig. 4.

The prominent hydrophilic nature of the flax fiber reinforced composites is identifiable by evaluating the diffusion coefficients during the desorption process, D_{des}. Indeed, the laminates reinforced by natural fibers show D_{des} values approximately five times higher than glass based ones, regardless the salt-fog exposition time (i.e., 15 and 30 days).

The presence of glass fibers in the stacking sequence of the investigated laminates has a marked effect in the desorption process (i.e., occurring during the dry stage) rather than in the sorption one (i.e., humid stage). In particular, glass fibers act as a shield against the water diffusion towards the bulk of the material, thus limiting the degradation phenomena in these composite laminate (in terms of interfacial debonding, delamination or microcracking). This can be confirmed by the low diffusion coefficient values shown by composites aged even for long aging times in the salt-fog chamber.

Different considerations can be argued for the FC laminate, where a progressive increase of D at increasing the exposure time to salt-fog is observed. This behavior can be ascribed to the greater degradation suffered by the composite reinforced with natural fibers. Indeed, it is widely known that long-term exposure to humid environmental conditions can lead to the formation of delamination, debonding voids or micro-cracks in natural fiber reinforced composites [47]. These defects represent preferential paths for the diffusion of water, which will desorb much faster from the bulk of the material [48].

Summarizing, both the reinforcement type and the staking sequence play a key role on the water retention and its release in composites exposed to the humid/dry aging cycles. In particular, the hybridization allows to achieve a balance between the hydrophilic behavior of flax fibers and the better stability in humid environments shown by glass fibers. Consequently, the HC batch, characterized by outer glass fiber reinforced layers, displayed an intermediate water absorption and desorption behavior among other laminates.

3.2. Flexural performances evolution during humid/dry cycle

In order to investigate the influence of the stacking sequence on the performances as well as on the stability of composites under different environmental conditions, it is first important to define how the mechanical behavior, in terms of stress-strain curve, varies for each type of laminate under humid/dry cycles (Fig. 5).

The figure shows the stress-strain curves for unaged flax (i.e., FC-H0D0), hybrid (i.e., HC-H0D0) and glass (i.e., GC-H0D0) composites. The average stress-strain curves, calculated by considering all the tests performed for each specific batch, are represented by solid line curves. Additionally, the colored areas illustrate the distribution of all achieved curves for each batch during the experimental campaign. Hence, this area indirectly indicates the data distribution along the strain evolution of the three-point bending test.

As expected, the stacking sequence plays a key role in the stress-strain curve: i.e., the presence of glass fibers allows for an increase in the strength and stiffness of the composite laminate. Indeed, the FC laminate, consisting only of flax reinforced laminae, has significantly lower strength and stiffness compared to the GC laminate, consisting only of glass reinforced laminae. The latter shows the best mechanical performances with average strength values above 350 MPa. The hybrid laminate evidences an intermediate behavior between the other types, although it shows stress-strain curves closer to those of GC-H0D0 batch. This behavior is due to the presence of glass fibers in the outer plies,

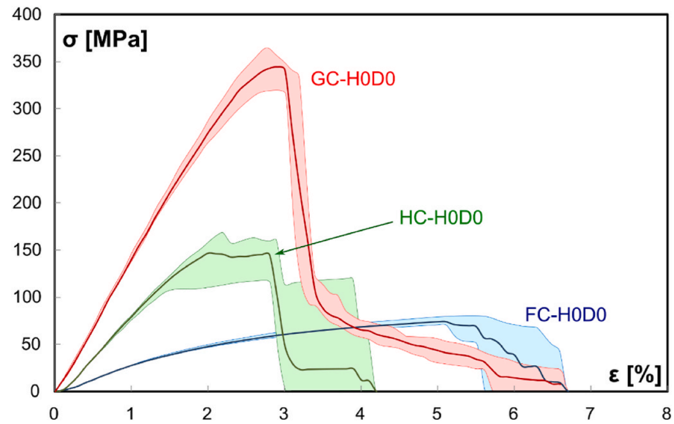

Fig. 5. Stress-strain curves of unaged flax (i.e., FC-H0D0) hybrid (i.e., HC-H0D0) and glass (i.e., GC-H0D0) fiber reinforced composites (data distribution evidenced in colored areas).

which offer a significant contribution to increase the flexural strength and stiffness of the laminate. At the same time, the proposed hybrid stacking sequence is potentially suitable for improving the aging resistance of the composite laminate under severe environmental conditions, thanks to the possible shielding action offered by the outer layer reinforced with synthetic fibers.

By evaluating the distribution of the curves recorded for each test batch, marked by the colored areas in the graph, further information can be obtained regarding the homogeneity and dispersion of the data. In particular, it is clearly identifiable that the GC-H0D0 laminates are characterized by a low dispersion of the data. The maximum stress value is relatively homogeneous in the range of 342–367 MPa. Similarly, the failure of the external fibers suffering tensile stress during the bending test, characterized by the sudden collapse of the load, is associated with a strain of about 3.3%.

Slightly different considerations can be drawn by analyzing the batch FC-H0D0, for which it is observed that the initial region of elastoplastic deformation is relatively narrow and regular. In correspondence with the strain at failure, there is a clear extension of the marked colored area (due to a large dispersion on curve trends).

This indicates that the specimens, although characterized by comparable values of stiffness and strength, are characterized by different strains at failure values. The region of progressive reduction of the stress is relatively wide indicating that the failure of the laminate takes place at different deformation values for the different samples, leading to a high dispersion of the data for this mechanical property.

Such a behavior can be attributed to the heterogeneous structure of flax fibers rather than the limited fiber-matrix adhesion in natural fiber composites, which has a significant effect on interlaminar shear stresses [49]. These stresses become relevant after the fracture of the tensile stressed lower layers and during the consequent propagation of the crack transversely to loading direction (longitudinally) [50]. As a result, there is a wider dispersion of the curve trends in the post-fracture phase.

In contrast to the other batches, the hybrid HC-H0D0 laminate exhibits a greater variability in the stress-strain curves, as evidenced by the relatively large colored area. At low levels of strain, the curve shows a linear trend with minimal variability, indicating a low dispersion of the elastic modulus (e.g. slope of the curve in this section of the graph). However, a greater divergence in the trend of the stress-deformation curves can be observed when the fracture occurs: i.e., the dispersion area is wide and it is further enlarged at larger strain values.

Overall, the hybrid composite clearly evidenced a wide dispersion in both maximum strength and strain at break. This behavior is believed to stem from inherent differences in the mechanical response of glass and flax fibers, which induces a high interlaminar stresses in the hybridization plane [51,52]. This represents the limiting factor of this type of composite, as confirmed by the slightly lower strain at break compared to that of GC one. In fact, the hybrid laminate experiences early fractures at an average strain value of approximately 0.25% lower than GC-H0D0.

An optimization of the hybrid stacking sequence could minimize this issue: e.g., by using laminae reinforced with randomly placed glass or flax short fibers should be used between the internal flax reinforced laminae and the external glass one. This approach will allow to reduce interlaminar stresses thus contributing to a better mechanical stability of the laminate.

The stress-strain curves of composite laminates first exposed to salt-fog for (a, c) 15 days and (b, d) 30 days and then dried for (a, b) 0 days (i.e., not dried) and (c, d) 21 days are illustrated in Fig. 6. It is noteworthy that the mechanical performances of all laminates gradually decrease with the exposure time in the salt spray chamber. Specifically, the natural fiber composites exhibit a significant reduction in the flexural strength (identified as the achieved maximum stress) as evidenced after 30 days of salt-fog exposition, with a decrease in the maximum stress for FC-H30D0 batch of about 31.5% compared to the unaged one (i.e., FC-H0D0).

Furthermore, it was observed that the hydrophilic flax laminate underwent a softening phenomenon caused by the absorption of water during the humid stage. As a result of this softening, there was a slight increase in the elongation at break, indicating an improvement in the material's deformability [53]. This behavior can be attributed to the moisture's effect on the composite's mechanical properties, which has been previously reported. Therefore, the water absorption of the hydrophilic flax laminate appears to have a significant impact on the material's overall performance, with implications for its potential applications.

By analyzing the data dispersion (colored areas in Fig. 6), it can be observed that the considerations previously discussed for unaged samples (i.e., low dispersion in GC, relevant dispersion in FC only in post-fracture and relevant dispersion in HC for almost the entire curve) can be confirmed. However, further analysis reveals that, due to aging cycle, the strain at break increased for laminates fully or partially reinforced by flax fibers (i.e., FC and HC batches). For these batches, an increase in both strain and post-fracture region is observed. Once the fracture is initiated (identified by the sudden load reduction), a progressive decay of performance is observed expecially for the hybrid laminate, attributable to an elastoplastic behavior of the matrix and natural fibers induced by aging in a humid environment. At the same time, the fracture strain also presents a greater variability, further amplifying the dispersion area in this region for FC and HC batches.

The micrographic details of the fracture surfaces of composites shown in Fig. 7 confirm these hypotheses. In particular, Fig. 7a shows that FC exhibits evident debonding and delamination phenomena inside the flax bundle, which are favored by large water sorption during the humid stage due to scarce interfacial adhesion between the natural fiber and the surrounding epoxy matrix. On the contrary, GC (Fig. 7c) exhibits more stable fiber/matrix interaction showing fiber bundles without evidence of relevant degradation phenomena except for a quite large crack located in the matrix, which can be probably ascribed to interlaminar shear stresses. Finally, HC (Fig. 7b) shows an intermediate morphology in comparison to the previous laminates (i.e., FC and GC). In more details, it can be noticed that the external glass reinforced layers, directly exposed to the environment, are quite homogenous with some local voids or debonding effects. Furthermore, the internal flax layers show the polymeric matrix still bonded with the fibers but also clearly frayed strands due to low interface adhesion, probably due to the relevant interlaminar stresses between the laminae characterized by different stiffness that could favor premature fractures along this plane.

In order to better discriminate, graphically, the different performances degradation and recovery of all the investigated laminates, a topological map based on mechanical properties (i.e., flexural strength and modulus) modifications during the aging cycle is proposed in Fig. 8.

The x axis index, defined as $(\varepsilon_i/\varepsilon_0 * E_0/E_i)^{0.5}$, highlights the effects of

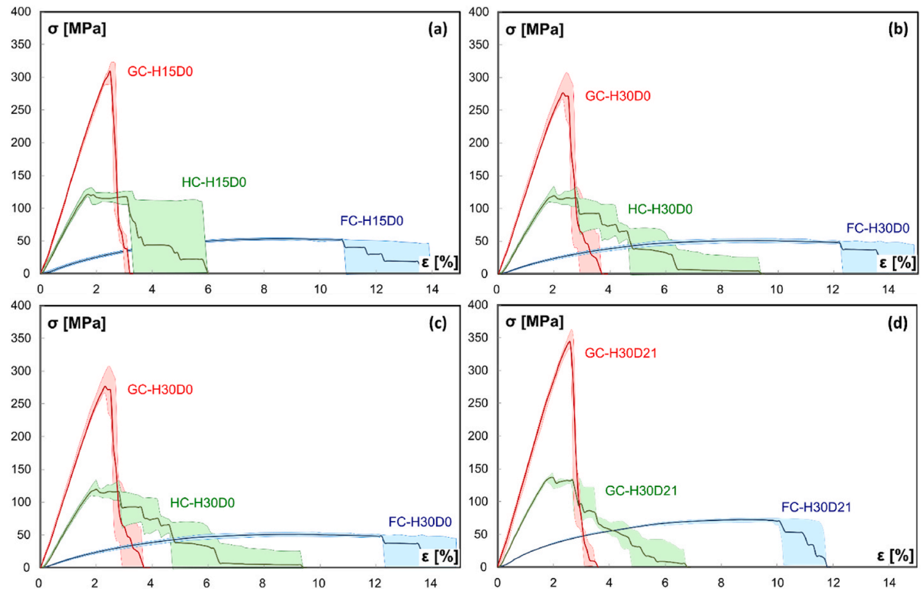

Fig. 6. Stress-strain curves of FC, HC and GC samples for different humid and dry conditions (data distribution evidenced by colored areas).

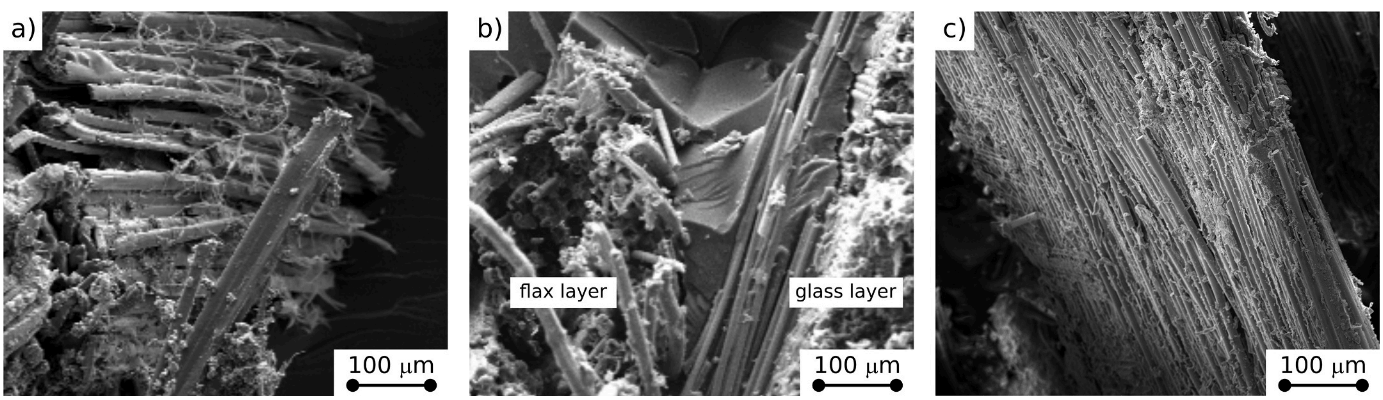

Fig. 7. Morphologies of the fractured surfaces of (a) FC, (b) HC and (c) GC samples at the end of the humid/dry cycle.

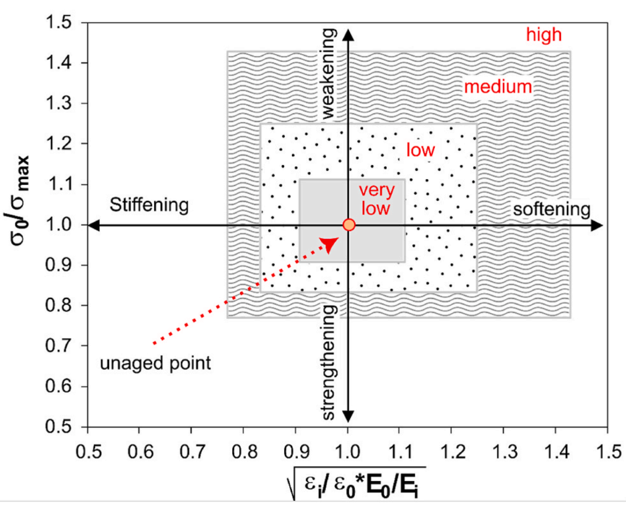

Fig. 8. Topological scheme of the σ_{max}/σ_0 vs $\varepsilon_i/\varepsilon_0{}^*E_0/E_i$ plot.

the aging cycle both on strain at failure ($\varepsilon_i/\varepsilon_0$) and stiffness ($E_0/E_i$.), where subscript 0 and i are referred to unaged and aged at time i samples, respectively. Thus, the higher the value, the greater the material's ductility is affected by the aging cycle. For this reason, it will be named in the next "softening index". The y axis σ_0/σ_{max} index, named in the next "weakening index", is chosen to assess the effect of the aging cycle on composites' strength. In particular, σ_{max} and σ_0 are the maximum stress values at generic time i and zero time (i.e., unaged samples), respectively. Values of both indices equal to 1, indicated as unaged threshold in Fig. 8, are referred to the unaged condition. The quadrant with x and y values greater than 1 identifies the softening and weakening zones, respectively. Similarly, lower values than 1 for the defined indices identify materials which experienced improvements of stiffness and strength during the aging cycle, respectively. The further is away from the origin of the axes (identified by both indices values equal to 1), referred as "unaged point", the greater the effect of environmental condition on the material's properties.

By using this topological map together with the acquired experimental results, Fig. 9 shows the evolution of σ_0/σ_{max} vs $(\varepsilon_i/\varepsilon_0{}^*E_0/E_i)^{0.5}$ for FC, HC and GC composites at varying the humid and dry times (red dotted lines indicate the unaged threshold in the figure).

This graph clearly shows that the presence of glass fibers in the stacking sequence induces a limited deviation from the initial unaged condition. In particular, batches GC and HC show a data distribution

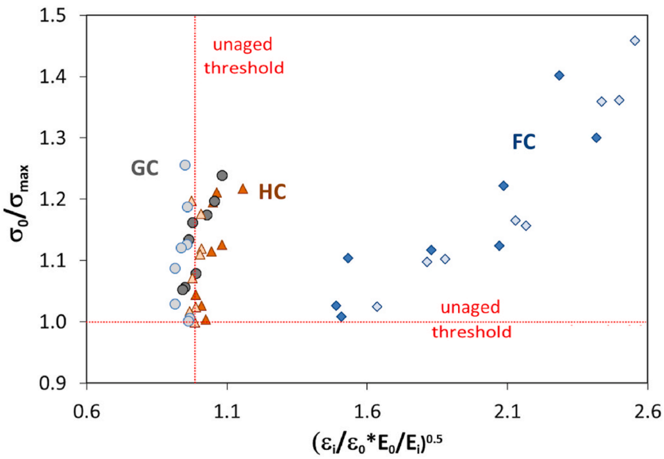

Fig. 9. Evolution of σ_{max}/σ_0 vs $(\varepsilon_i/\varepsilon_0*E_0/E_i)^{0.5}$ for FC, HC and GC samples at different humid and dry conditions.

very close to the unaged point. A distribution of the experimental data, during drying time, parallel to the y-axis indicates that the aging cycle has limited effects on the materials' ductility. On the other hand, a performance decay effect is observed in terms of strength, thus indicating an evident weakening of these materials. However, the samples recover their mechanical performances during drying, i.e., they are able to regain values of both indices close to the initial ones (i.e., unaged state). Conversely, batch FC evidences clear effect of the aging cycle on both strength and ductility. The aging cycle in the salt-fog environment triggers softening and weakening effects on the mechanical performances of the composite. After drying, the trend tends towards the unaged condition. However, there remains a clear shift on x axis attributable to the presence of permanent ductility in the material, which persists even after long drying times. These results further confirm the previously discussed considerations about the different behavior of synthetic and natural fibers in the presence of humid environments, which plays a key role in the aging resistance of composites aged under alternate humid/dry cycles.

The hybridization through external glass fiber reinforced layers of flax laminates leads to significant improvement in the material's stability and durability in severe environmental conditions. In particular, in terms of performances decay and subsequent recovery ability, no significant differences are observable between GC and HC specimens. These findings confirm the significant applicative potential of hybridized composite laminates when structural or semi-structural components need to be used under severe environmental conditions such as outdoor applications.

Based on these considerations, a schematization of the topological weakening/softening map can be made for the investigated composites (Fig. 10). It can be noted that hybrid composites, at the end of the humid stage and during the recovery in the dry stage, operate in mechanical conditions close to those of the laminate reinforced with synthetic fibers (i.e., GC). The hybridization induces a marked discontinuity on the aging behavior of the natural fiber laminate inducing an evident stabilization of the performances. As expected, the dry stage has a more marked effect on FC laminate, since the latter shows greater tendency to absorb water if exposed to humid or wet environments. However, while hybrid laminates are able to converge towards the unaged point thus evidencing a relevant performances recovery, composites reinforced with natural fibers laminates preserve a residual softening at the end of the dry stage. On the other hand, the latter also recovered the weakening degradation experienced during the humid stage. This finding indicates that the weakening induced during the humid stage is related to reversible mechanisms, whereas the softening is related to irreversible ones.

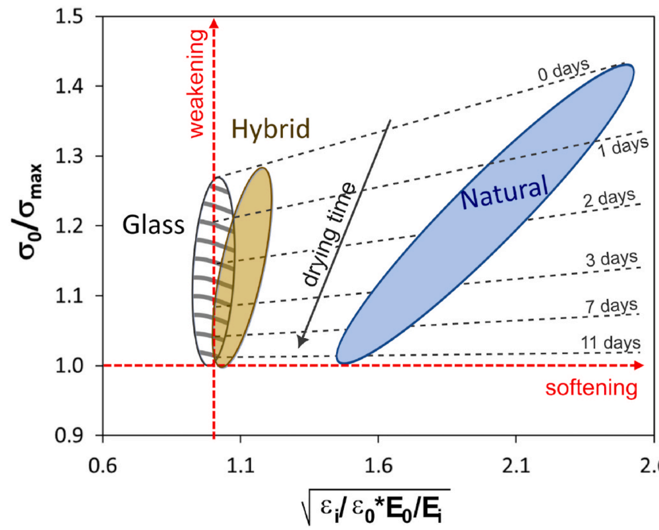

Fig. 10. Schematization of topological weakening/softening map for flax, flax-glass hybrid and glass fiber reinforced composites.

Future developments will be aimed at evaluating the effectiveness of the map for other laminate configurations. Moreover, it will be investigated to increase the exposure time of the wet stage and evaluate how this parameter can influence the ratio of the reversibility and irreversibility of the weakening and softening processes in the aged composites. In this concern, the improvement of knowledge about the effect of cyclic humid/dry aging tests in order to assess whether this high mechanical reversibility of hybrid flax-glass laminates persists even for greater number of aging cycles could be ab added value to discriminate reversible/irreversible weakening/softening phenomena in the composite laminates.

In this context, the improvement of knowledge about the effect of cyclic humid/dry aging tests to assess if the mechanical reversibility of hybrid composites persists even for greater number of cycles could represent an added value to discriminate reversible/irreversible weakening and softening phenomena.

4. Conclusions

The aim of the present paper is to analyze how the exposition to an aging cycle consisting of an initial humid stage (i.e., exposure to salt-fog at 35 °C for 15 and 30 days) followed by a "dry" stage (i.e., 50% R.H. and 23 °C for 21 days), can influence the mechanical stability of epoxy-based laminates reinforced with flax, glass and flax-glass hybrid fibers by using a topological weakening and softening map as simplified tool.

In particular, the proposed map has proven to be able to graphically discriminate the reversible and irreversible degradative phenomena that influence the mechanical response of the investigated composites. In particular, this simplified tool allows to evidence that hybrid flax-glass composites show a behavior very close to that of full glass ones: i.e., the humid stage causes a strength reduction of about 25%. However, this mechanical decay is almost fully reversible because both HC and GC laminates, which exhibit a nearly complete recovery of their performances at the end of the dry stage. Conversely, by analysing the topological map it can also be noticed that the FC laminate undergoes both weakening and softening phenomena (i.e., reduction of the strength and stiffness indices of about 1.46% and 2.56%, respectively), which cannot be fully recovered at the end of the dry stage (i.e. partially reversible).

Lastly, future research activities will be focused to validate the proposed map in order to better assess the performances decline and recovery during multiple humid/dry cycles, furthermore amplifying the application and design capability of this simplified approach.

CRediT authorship contribution statement

L. Calabrese: Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing – original draft, Writing – review & editing. **V. Fiore:** Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing – original draft, Writing – review & editing. **A. Valenza:** Supervision, Resources, Project administration, Funding acquisition. **E. Proverbio:** Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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