# Assessment of performance degradation of flax-glass hybrid fiber reinforced composites during a salt spray fog/dry aging cycle

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## Abstract

The main goal of this paper is the evaluation of the performances reversibility of hybrid composites when they are dried after being aged in salt-fog environment. To this aim, epoxy composites reinforced with flax and glass fabrics respectively in the internal and external laminae were at first exposed to salt-fog (i.e., identified as wet phase) and then stored in controlled conditions (i.e., identified as dry phase). The flexural properties evolution of these composites as well as their water uptake and contact angle were monitored at varying time of both phases. The flexural strength and modulus of hybrid composites is 23.4% (17.9%) and 15.5% (12.9%) lower than unaged ones after 30 (15) days of salt-fog exposition, respectively. However, the dry phase allows an almost complete recovery of the composite performances. In particular, samples exposed to salt-fog for 30 days show an adequate recovery in the stiffness at the end of the dry phase, whereas their strength is about 10% lower than unaged ones.

**Keywords**: A. Polymer-matrix composites (PMCs); B. Environmental degradation; D. Mechanical testing; Moisture desorption, hybrid composites

# 1 Introduction

It is widely known that one of the main drawbacks that limits the use of natural fiber reinforced composites is their scarce durability in humid or wet environments such as marine one [1] [2] [3]. Due to this, wide efforts were made by various researchers in order to find solutions for using these promising materials even for components exposed to aggressive conditions [4] [5] [6] [7]. In this context, a wide literature was focused on hybrid composites in the last years: i.e., polymeric materials reinforced with natural fibers together with synthetic fibers that are stronger, less hydrophilic and more stable in severe environmental conditions [8]. The presence of synthetic fibers in addition to the choice of adequate stacking sequences allow to obtain composites having better mechanical properties as well as with improved aging resistance. These findings were highlighted for the first time in an our previous paper [9], aimed to evaluate the influence of external basalt layers on the durability in marine environment of flax fiber reinforced composites. Quite similar results were obtained by comparing the effect of two different staking sequences (i.e., intercalated and sandwich-like) on the aging resistance of jute-basalt hybrid composites [10].

In this regard, Cheour et al. [11] studied the long-term water immersion of flax-glass hybrid composites showing that the water saturation is reached after about 25 days and 10 months for hybrid composites with flax or glass fibers as reinforcement of the outer layers, respectively. Moreover, the flax-glass hybrid laminate with two inner flax layers and two outer glass layers was the best one where damping and bending modulus are the main criteria.

The bearing behavior of flax-glass pinned composites was also investigated showing that the presence of external glass reinforced layers in flax/epoxy composite positively influences the mechanical performance of mechanically fastened joints [12] as well as their durability in marine environment [13] [14].

From all these results, it is quite evident that the aging resistance of natural/synthetic fiber reinforced hybrid composites can be improved by reinforcing the external laminae with synthetic fibers (i.e.

glass, basalt, carbon), which thereby acts as shield for the internal layers against the surrounding degradative environment. Nevertheless, it is worth noting that the effect of the stacking sequence on the evolution of the mechanical response of hybrid composites during aging strictly depends on which mechanical property is considered. For instance, Selver et al. [15] evidenced that the stacking sequence does not significantly affect the tensile properties of hybrid flax/glass and jute/glass composites whereas it noticeably alters their flexural properties as well as their dynamical properties. In particular, it was confirmed the best flexural and damping properties were found for hybrid composites having the outer laminae reinforced by glass fibers. Moreover, Sarasini et al. [16] showed that better impact performances of carbon/flax hybrid composites subjected to low velocity impact can be achieved by stacking flax fiber reinforced layers as outer laminae and carbon as inner ones.

In spite of their low resistance against humid or wet conditions, natural fiber reinforced composites are able to partially recover their performances under discontinuous exposition to marine environment. This finding was clearly highlighted in our recent paper [17], whereby it was shown that flax fiber reinforced composites exposed to salt-fog condition for 30 days regain more than 98% and nearly 69% of their initial flexural strength and modulus values after 21 days of drying, respectively.

Similarly, the present paper aims to investigate the recover capability of flax-glass hybrid composites with glass reinforced layers as external shield of the internal flax reinforced ones. To this scope, hybrid composites was initially aged in salt-fog spray condition respectively for 15 and 30 days, before being stored in dry condition (i.e., 50% R.H. and 22 °C) for an interval time of 21 days.

# 2 Experimental

## 2.1 Materials and Methods

Hybrid composite panels (30 cm x 30 cm) were manufactured through vacuum infusion technique, by curing them at room temperature (i.e., 25 °C ± 1°C) for 24 h. Then, a post-curing process (i.e., 50

°C for 15 h) was carried out according to the technical datasheet of the epoxy resin (SX8 EVO by Mates Italiana s.r.l., Milan, Italy) used as matrix.

Two fabrics were used as reinforcement of hybrid composite panels: i.e., the first one is a 2 × 2 twill weave woven flax fabric with nominal areal weight 318 g/m$^2$ supplied by Lineo (Saint Martin du Tilleul, France), the second one is a plain weave woven glass fabrics with nominal areal weight 200 g/m$^2$) supplied by Mike Compositi (Milano, Italy). In particular, 8 reinforced layers were used as reinforcement and the stacking sequence of hybrid composites is (G2/F2)s, where F and G are referred to the internal flax reinforced layers and the external glass layers, respectively.

## 2.2 Salt-fog/dry aging phases

With the aim to assess how the mechanical performances of hybrid composites aged in humid or wet conditions (such as a marine environment) can be reversibly recovered thanks to a dry phase, the composite panels were initially exposed to salt-fog spray conditions in a salt spray chamber model SC/KWT 450 by Weiss (Buchen, Germany) for 15 and 30 days, respectively. This phase (i.e. wet phase in the next) was conducted by setting the temperature inside the chamber equal to 35°C as well as by filling the reservoir of the chamber with an aqueous solution of NaCl (5% in weight), according to the ASTM B 117 standard.

At the end of this initial phase, five specimens for each investigated aging time were cut to their nominal dimensions by using a diamond blade saw. Afterwards, the aged specimens were stored in dry conditions (i.e., 50% relative humidity and 22 °C temperature) up to 21 days, before carrying out the mechanical tests. The latter phase will be indicated in the next as dry phase.

Depending on salt-fog exposition and drying times, all batches were codifyed with a "HW$t_w$D$t_d$" code, where $t_w$ and $t_d$ are the time intervals in days of (i) wet and (ii) dry phases, respectively. For instance, HW30D7 code indicates samples exposed to salt spray fog for 30 days and then dryed for 7 day. Analogously, HW0D0 code is referred to unaged samples (i.e., reference).

## 2.3 Water uptake

The water uptake evolution of hybrid composites was evaluated during wet and dry phases according to ASTM D570 standard. During the wet phase, two square laminates (100 mm × 100 mm) were periodically withdrawn from the salt-fog chamber, wiped with a dry clean cloth and weighed. During the dry phase, the weight of HW15 and HW30 batches was monitored to assess the mass recovery aptitude of the hybrid laminates under controlled environmental conditions.

The water uptake ($M_t$, in percentage) of hybrid composites was expressed at varying time intervals as:

$$M_t(\%) = \frac{W_{t-}W_0}{W_0} \cdot 100 \qquad \textbf{Eq. 1}$$

Where $M_t$ is the percent of water uptake. $W_0$ and $W_t$ denote the weight of the unaged and aged at the exposure time t, respectively.

## 2.4 Density and void content measurements

Density measurements were carried out on unaged and aged samples (i.e., HW15 and HW30 batches) at the end of the wet phase and during the dry phase. A helium pycnometer (Ultrapyc 5000 foam by Anton Paar, Graz, Austria) coupled with a weight measurement (using the same analytical balance exploited for the water uptake monitoring) was used to calculate the apparent density of the composites ($\rho_{ac}$). For each sample, 10 replicas were performed.

The theoretical density of the composites ($\rho_{tc}$) was determined, by using the mixture rule:

$$\rho_{tc} = \frac{1}{\sum_{i=1}^{n} W_i/\rho_i} \qquad \textbf{Eq. 2}$$

Where, W and $\rho$ are the weight fraction and density, respectively. In the summation, the subscript $i$ is referred to the composite constituents (i.e., matrix, glass and flax fibers). Finally, according to ASTM D2734 standard, the volume fraction of voids ($V_V$) was calculated, by using the following equation:

$$V_V = \frac{\rho_{tc} - \rho_{ac}}{\rho_{tc}} \qquad \textbf{Eq. 3}$$

### 2.5 Wettability measurements

The evolution of the static water contact angle (WCA) of hybrid composites has been monitored during the wet phase by the sessile drop technique through an Attension Theta tensiometer instrument (Biolin Scientific, Gothenburg, Sweden). All measurements were performed at 25 °C and open to air conditions. The surface of composite samples was cleaned with a dry before contact angle measurements. The WCA was measured in ten different positions of each sample, equally dispersed on the surface, to guarantee a suitable accuracy of the data.

### 2.6 Three-point bending tests

Five composite samples (13 mm x 64 mm) for each investigated condition were tested in three-point bending configuration by using a U.T.M. model Z005 (Zwick-Roell, Ulm, Germany) equipped with 5 kN load cell. The mechanical tests were performed following the ASTM D790 standard, by setting the support span and crosshead speed equal to 54 mm and 1.4 mm/min, respectively.

### 2.7 Morphological analysis

The surface of the fractured specimens was evaluated coupling a digital optical microscope (model KH8700 3D digital microscope by Hirox, Tokyo, Japan) analyses. In particular, for SEM analysis, all samples were preliminary, graphite sputtered in order to avoid electrostatic charging phenomena under the electron beam.

# 3 Results and discussion

## 3.1 Water uptake

Figure 2 shows the evolution of the water uptake of hybrid laminates during the wet/dry phases. In particular, the dark and light markers are referred to specimens aged in the salt-fog chamber for 15 and 30 days, respectively (i.e., HW15 and HW30 batches).

During the wet phase, it is worth noting that a progressive increase of the water uptake takes place. In accordance with the water absorption phenomena, a linear proportionality between the water uptake and the exposure time can be observed during the initial phase of the process (i.e., see trend of HW15 batch in Figure 2). For longer exposure times (i.e., see HW30 batch trend), it can be noticed a deviation from the linearity: e.g., a progressive reduction in the $\Delta M_t/\Delta t$ slope towards a slight asymptotic trend. In particular, HW30 batch exhibited a maximum water uptake of 4.79% after 30 days (i.e. 720 hours) of salt-fog exposure.

However, it is worth noting that the curve trend does not show a plateau at the end of the wet phase: i.e., the slight slope of the curve for long exposure time suggests that the absorption process is not yet completed. This finding can be ascribed to the shielding role played by the outer glass reinforced laminae which protect the inner hydrophilic region (i.e., flax reinforced laminae) of the laminate towards the diffusion of the water molecules. The barrier action offered by the external protective layers allows hybrid composite to reach at least one-half maximum water uptake values compared to full natural flax composites [18].

Consequently, the water absorption phase shows a bilinear trend with a knee at nearly 360 hours of exposure time to salt-fog.

In the humid environment, the water molecule diffusion through the free volume of the laminate occurs at short aging time. The presence of voids, structural or interstitial cavities represent preferential paths for the water diffusion. This process, identified as free water diffusion, is kinetically fast as well as it plays a key role in the initial water uptake of composites [19] [20]. However, the

water permeation in the laminate and the resultant filling of the free spaces in the material bulk do not involve significant swelling phenomena [21]. Consequently, it is believed that this process is not particularly critical in term of residual damage [22].

Together with the progressive wet phase, the kinetic of free water diffusion decreases due to the reduced number of empty sites remaining in the structure. The knee in the water uptake trend is overcome: i.e., the absorption of free water is hindered due to longer exposition times. In this, the water absorbed in the laminate could be classified predominantly as bound water [20] [23]. The water molecules interact with the polar groups present on the reactive sites of the composite constituents forming hydrogen bonds [3]. This process is much slower than that relating to free water, consequently there is a reduced slope of the curve. It is widely known that glass fibers show lower affinity with water molecules than cellulosic one such as flax, implying better stability in humid or wet environments [24] [25].

Concerning the dry phase, the water uptake trend shows a clear inversion trend. In particular, both batches (i.e., HW15 and HW30) exhibit a relevant weight decrease already after few drying days. As reference, the water uptake of HW15 batch decreases of 0.83% after 1 day (i.e., from 4.11% to 3.27 % for HW15D0 and HW15D1, respectively). Analogously, for batch a decrement of 0.87 % in the water uptake was experienced by HW30 composites after 1 day (i.e., from 4.79 % to 3.92% for HW30D0 and HW30D1, respectively). Finally, a water uptake plateau can be identified at longer drying time for both the investigated batches. In more detail, HW30 batch shows twice the residual water uptake of HW15 at the end of the dry phase (i.e., $M_t$ ~ 0.71 % and ~ 1.80 % for HW15 and HW30 batches, respectively). This finding confirms that the absorbed water can be reversibly desorbed with a quite fast process. However, non-reversible absorption processes are triggered due to the long exposition to salt-fog during the initial wet phase. This suggests that local degradative phenomena, induced by the water absorption, have promoted permanent degradative processes, which persist even after long drying times.

It is worth noting that the curve trend during the dry phase is fairly similar regardless the exposition time to salt-fog (i.e., wet phase). Indeed, both batches (i.e., HW15 and HW30) experienced a quite fast weight decrease in the early stage of the dry phase that progressively stabilizes at longer drying times. This result can be considered surprising by considering that the desorption kinetic during the dry phase of full flax fiber reinforced composites increased with the exposition time to salt-fog (i.e., the wet phase) [17]. Moreover, it is important to point out that hybrid composites show lower water uptakes at the end of the wet phase in addition to slower desorption during the dry phase in comparison to flax composites, regardless the time duration of the wet phase (i.e., 15 or 30 days).

In order to get further insights on the correlation between the degradative phenomena and the water uptake experienced by hybrid composites, their apparent density and void content evolution were evaluated at varying wet/dry condition (Figure 3).

The density of hybrid composites is clearly influenced by the aging phase. In more detail, the exposition time during the wet phase involves density increases of about 3.9% and 4.4% for HW15D0 and HW30D0 batches compared to the unaged composite (i.e., HW0D0), respectively. A progressive water absorption occur in the hydrophilic areas or in the porosity of the laminates, thus implying a void reduction and an increase in the bulk composite density [26]. Furthermore, during the drying phase, the absorbed water evaporates, increasing the free volume of voids and defects. This jointly implies an increase in the void content and a reduction in the bulk density of the laminate. The HW15D21 and HW30D21 batches exhibit a bulk density of 1.37 g/cm$^3$ and 1.38 g/cm$^3$, respectively. On the other hand, the void content experienced a different trend. In particular, this parameter decreases due to salt-fog exposition from 6.1% (unaged HW0D0) to 5.2% and 5.3% for HW15D0 and HW30D0 batches, respectively. This behavior can be ascribed to the swelling as well as to the absorbed free water phenomena which reduce the free volume of voids, cracks and delamination created during the wet phase [27]. During this phase, a significant increase in the voids content can be noticed, probably due to the water evaporation, which leaves empty cavities and cracks in the

laminates. In particular, the maximum void content was observed for the HW30D21 batch (i.e., about 6.3%).

### 3.2 Surface wettability

The WCA values experienced by hybrid composites at different wet/dry interval times are reported in Figure 4. The horizontal red dotted line (set at 90°) identifies the transition from hydrophilic to hydrophobic behavior of the surface. A clear influence of the wet or dry phase on the interaction between water and the composite surface can be identified. In particular, three stages can be distinguished:

1. *Unaged*: The HW0D0 batch is characterized by an average WCA of 97.7°, evidencing a marked hydrophobic behavior. The hybrid laminate is reinforced by hydrophilic flax fabrics and glass ones characterized by a less relevant interaction with water molecules. The latter, being the external skin of the hybrid composite, offers a shielding action against the water diffusion. Likewise, it acts positively in increasing the hydrophobic nature of the surface. Furthermore, the thermosetting matrix surrounding the reinforcing fibers enhances the shielding action supplied by the outermost layers, thus preventing a direct interaction of the inner layers with the water. This aspect has clearly a crucial role in the activation or delay of the superficial absorption phenomena.
2. *Wet phase*: it is worth noting that hybrid composites show a significant reduction in the static WCA due to the exposition to salt-fog. The hydrophobic nature of the fiberglass external layers is partially affected already after 15 days in the climatic chamber. In fact, the HW15D0 batch shows a contact angle of 94.4°, almost close to the hydrophilicity threshold of 90°. Concurrent degradative mechanisms can synergistically influence the surface properties of the laminate: i) a supplementary post-cure treatment occurs due to the temperature (i.e., 35 °C) inside the climatic chamber [28]. Consequently, the laminate achieves a higher conversion degree, thus reducing the water diffusion and potentially increasing the hydrophobic

properties of the surface [29]; ii) local dissolution and swelling of the thermosetting resin promote the triggering of local surface defects and cracks [30]; iii) the water diffusion by capillarity along the fiber-matrix interface, coupled to their differential swellings, could create internal interfacial stresses [31] that in turn favor the formation of cracks on the outermost laminae, directly exposed to the aggressive environment. The formation of these local superficial defects increases the affinity between the external laminae and the water molecules, thus accelerating the diffusion of water towards the inner laminae of the laminate. This effect is further amplified for longer exposure times in the humid environment. In fact, the WCA of HW30D0 sample is about 7° lower than that of HW15D0 one (i.e., 87.2° versus 94.4°). Furthermore, HW30D0 laminate shows WCA slightly lower than 90° indicating a hydrophilic behavior of the surface. For long exposition time to salt-fog, it is possible to hypothesize that the shielding action provided by the epoxy matrix as well as by glass fibers is partially compromised. Hence, the internal flax fibers can contribute to increase the surface hydrophilicity of the hybrid laminate [9] [32]. In this regard, a relevant role is surely played by the sodium chloride in the salt-fog, which leads to salt crystals deposit on the composite surface asperities such as voids, defects and cavities. Hence, the water diffusion capability in the composite laminate enhances due to hydrophilic behavior of sodium chloride. This further increases the presence of surface defects and cracks triggering an autocatalytic degradative phenomenon [33,34].

3. *Dry phase*: as shown in Figure 2, a significant weight reduction takes place during the dry phase, due to the evaporation of the water absorbed during the wet phase. Similar to absorption/desorption results, the composite laminate shows a relevant recovery of the hydrophobic properties observed in the unaged batch. However, by comparing unaged and wet/dry aged samples (i.e., those initially exposed to salt-fog and then stored in dry conditions), a residual mismatch in the water contact angle of about 5 ° (i.e., 97.7° versus 92.1° for HW0D0 and HW30D21 batches, respectively) is observed. This result suggests that

not all the water absorption phenomena involve reversible degradative mechanisms. In addition to softening effect, the thermosetting resin can suffer degradative phenomena in local area with low cross-linking degree. These regions, due to a large amount of unreacted compounds, have a more marked hydrophilic behavior and tend to be more easily degraded in humid environments [35]. This leads to the formation of preferential paths for the diffusion of water which could reach the internal flax laminae [36] [37]. Moreover, cracks and voids are created on the surface, defects that irreversibly remain on the surface even after the evaporation of water occurred during the dry phase. Finally, the wet/dry aged samples (i.e., HW15D21 and HW30D21) show a greater affinity with water than the unaged one (i.e., HW0D0) confirming the partial irreversibility in surface properties of aged samples.

It can be noted that the WCA results of wet samples (i.e., HW15D0 and HW30D0) are characterized by larger error bar, which means higher dispersion of the data. This can be ascribed to the synergistic degradative mechanisms that trigger softening, weakening or surface damaging. The consequent formation of surface defects, voids or cavities enhances the structural heterogeneity of the composite, thus leading to the high dispersion of the water contact angle data. As expected, this effect is more relevant for HW30D0 samples than HW15D0 ones since it is strictly related to the exposition time to salt-fog.

### 3.3 Three-point bending tests

In order to assess the mechanical stability of the hybrid laminate in salt-fog environment (i.e., wet phase), the typical stress-strain curves of unaged (i.e., HW0D0) and aged (i.e., HW15D0 and HW30D0) samples were initially compared (Figure 5). By observing this figure, it can be drawn that the laminate shows a progressive reduction of its mechanical performances with increasing the exposition time in the climatic chamber. In particular, a marked reduction in the maximum stress can be observed already after 15 days of salt-fog exposition (i.e., about 18% lower than that of unaged samples). In addition, the composite stiffness, which can be associated with the slope of the initial

section of the stress-strain curve, evidences a gradual reduction at increasing the salt-fog exposition time. Furthermore, it should be noticed that the hybrid laminate experiences a slight increase of the elongation at break too, particularly after reaching the maximum load (i.e., in the post-peak zone). This behavior can mainly be attributed to the water absorption of the hybrid laminate during the salt spray test [38].

Due to the hybrid structure of the laminate, the effect of aging phenomena induced by the water absorption on the mechanical performances are manifold. They are indeed influenced by the greater or lesser durability of the various constituents of the composite laminate in a humid environment.

Flax fibers, due to their hydrophilic nature, are prone to degrade easily in critical environmental conditions such as marine one [2]. In fact, the exposure to humid environments leads to a fast swelling and degradation of natural fibers thus triggering fiber/matrix debonding and, as a consequence, decrements of composites strength and stiffness [39] [40].

Also synthetic fibers experienced some form of physical damage and/or chemical degradation when exposed to seawater or similar environments [41] [42]. Nevertheless, due to their mineral composition, these fibers offer greater resistance to the attack of both water and salt than natural fibers [2]. As consequence, glass fiber reinforced composites evidenced a more stable hydrophobic behavior than flax ones [43].

Finally, epoxy resins represent, among thermosetting polymers, one of the best choice as matrices for fiber reinforced composites which have to retain their mechanical and physical performances in hostile conditions, thus experiencing slight degradation when immersed in seawater [44].

In order to better understand the effect of the dry phase on the behavior of the investigated hybrid composite, some typical stress-strain curves of unaged, wet aged (i.e., exposed to salt-fog) and wet/dry aged samples are shown in Figure 6. These graphs clearly evidence the reversibility of the flexural properties of hybrid composites when they are dried after already being aged in salt-fog for 15 days (i.e., HW15Dt$_d$ samples) and 30 days (i.e., HW30Dt$_d$ samples).

Indeed, hybrid samples are able to regain partially stiffness (associated with the slope of the initial section of the stress-strain curve) as well as ultimate strength during their storage in controlled conditions, regardless the exposition time in the climatic chamber. More in detail, Figure 6 (a) shows that the stress-strain curve of HW15D21 sample is almost overlapped to that of unaged sample. This means that the hybrid composite previously exposed for 15 days to salt-fog, experiences an almost complete recover of their flexural properties after 21 days of storage in controlled conditions. Furthermore, it is interesting to notice that this recover is not just related to the beginning part of the stress-strain curve (i.e., the elastic branch up to the maximum strength) but it also concerns the post-peak behavior of the sample.

A similar trend has been also observed for samples exposed to salt-fog for 30 days, as shown in Figure 6 (b). The dried samples regain their mechanical performances, thus approaching gradually the behavior of unaged samples at increasing the time duration of the dry phase. Nevertheless, it is also important to point out that the HW30Dt$_d$ samples (i.e., those exposed to salt-fog for 30 days) are able to regain their performances in less extent than HW30Dt$_d$ samples. This means that the longer is the exposition to the humid environmental conditions, the lower is the recover capability of the hybrid material during the subsequent dry phase.

In order to quantify the reversibility of the mechanical properties of hybrid composites, the evolutions of their flexural strength and modulus at varying the time of both phases (i.e., wet and dry) are presented in Figure 7 (a) and (b), respectively.

### 3.4 Degradation map

The previous considerations show that the degradative phenomena induced by the aging cycle (i.e., wet and dry phases) have different effects on the flexural properties (i.e., strength and stiffness) of the hybrid composite. In order to better highlight how aging affects these mechanical parameters, two degradation indices, have been introduced. In particular, the strength degradation ($\sigma_{DI}$) and the stiffness degradation ($E_{DI}$) indices were defined according to the following expressions:

$$\sigma_{DI} = (\sigma_0 - \sigma_i)/\sigma_0 \qquad \textbf{Eq. 4}$$

$$E_{DI} = (E_0 - E_i)/E_0 \qquad \textbf{Eq. 5}$$

Where $\sigma_0$ and $E_0$ are the average strength and modulus values of unaged samples, respectively. $\sigma_i$ and $E_i$ are the same properties of aged composites at the i-th drying time interval, respectively. Therefore, these indices provide information on the percentage loss of the performance. The closer these indexes are to zero, the greater is the recovery of the mechanical characteristic during the dry phase. Vice versa, the greater the indices, the more relevant are the irreversible phenomena that degraded the specific characteristic (i.e., strength or stiffness).

Figure 8 shows the evolution of $\sigma_{DI}$ versus $E_{DI}$ in a cartesian plot. It is worth noting that both HW15 and HW30 batches show a monotonous trend with a progressive reduction of the indices, related to the recovery of the mechanical performances at increasing the drying time (i.e., see black arrow in Figure 8 for the drying time direction). Both curves show a sigmoidal trend with three well-defined zones and, taking into account the mismatch between the recovery trends of the two investigated batches, interesting information can be acquired on the experimental evidences occurring during the dry phase.

The points in the lower left corner of the graph are referred to the samples that did not undergo drying phase (i.e., HW15D0 and HW30D0). Therefore, this region can be associated with the beginning of the dry phase. It can be noticed that, due to long exposure times in salt-fog environment, there is a reduction in the strength and stiffness indices, with the first predominating over the second one. This behavior is attributable to the softening phenomena triggered during the wet phase. As previously discussed, the absorption of water induces the softening both of polymeric matrix and hydrophilic fibers together with the weakening of the interfacial adhesion due to the water permeation at the fiber-matrix interface [4] [45]. All these events affect the performances of the hybrid composite, which suffers significant reductions in both the flexural properties (i.e., strength and modulus).

Moving to the analysis of the effect of the dry phase, it is worth noting that the initial slope of the HW30 curve is higher than HW15 one. This can be ascribed to the higher absorbed water during the

wet phase, which can be reversibly released from the samples in the early stages of the dry phase. However, the HW30 markers always remain below the HW15 ones: i.e., the samples exposed to salt-fog for 30 days are not able to regain enough their performances during the dry phase up to reach the HW15 batch.

At increasing the drying time, both curves show a knee beyond which a significant increase in their slope can be noticed. Both indices decrease significantly due the relevant recovery of performances experienced by hybrid composites. This is referred as the transition zone of the samples toward a dry state.

At long drying time, a progressive stabilization of the indices occurs (highlighted by the reduction of the slopes of the curves). The HW15 batch shows a residual $\sigma_{DI}$ and $E_{DI}$ indices equal to 0.004 and 0.005, respectively. These final values suggest that 15 days in the climatic chamber were not enough to trigger irreversible degradative phenomena. This means that the water absorption in the wet phase involved the softening of the hybrid composite without starting the formation of defects (i.e., voids or cracks) which irreversibly compromise the mechanical performances at the end of the dry phase.

On the other hand, HW30 batch experiences a more evident residual mechanical decay. In particular, these samples have shown at the end of the drying phase $\sigma_{DI}$ and $E_{DI}$ values equal to 0.10 and 0.02, respectively.

Furthermore, it should be noticed that the HW30D21 samples show an adequate recovery in stiffness whereas their flexural strength at the end of the dry phase is significantly lower than the unaged ones (i.e. HW30D0). This is plausible by considering that the higher the exposure time, more likely irreversible degradative phenomena happen. In this case, the material irreversibly degrades due to e.g. voids, cracks and delamination triggered during the exposition to salt-fog environment. These do not significantly affect the stiffness of the hybrid composite but they play a key role in the stresses concentration at the crack tip or at fiber-matrix interface, thus favoring premature failures of the laminate at lower stress levels.

Further information can be acquired by analyzing the failure mechanisms occurred during wet and dry phase (see front and bottom view in Figure 9).

First of all, it can be noticed that the unaged sample (i.e., HW0D0) experienced a catastrophic failure. In particular, the crack starts in the outer bottom glass laminae, characterized by the maximum tensile stress. Afterwards, it propagates towards the middle zone of the laminate, orthogonally to the specimen length (i.e., longitudinally to the applied load direction). A large laceration of the fiber fabric with local debonding and delamination can be seen near the neutral axis, mainly ascribed to the stress gradient at the interface between glass (i.e., acting as skins) and flax laminae (i.e., acting as core). The sudden nature of this fracture is confirmed by the final failure found in the upper glass reinforced lamina in contact with the bending punch.

On the other hand, the hybrid samples exposed to salt-fog for 15 days (i.e., HW15D0) are characterized by a larger amount of secondary cracks which propagate orthogonally to the load direction. This experimental evidence is all the more marked the greater the exposure time in the climatic chamber (see HW30D0 sample in Figure 9). In more detail, the composite laminates suffered a larger plasticization phenomenon due to the water diffusion toward the internal flax laminae. A partial crack propagation takes place perpendicular to the applied load. This is due to the reduction of the interfacial adhesion at the matrix-fiber interface that promote delamination and interlaminar shear fractures.

The degradation phenomena led to a reduction in the laminate performances in addition to influence the fracture mechanisms by activating premature secondary fractures. However, as previously discussed, the performances decay is due to coupled reversible and irreversible aging mechanisms. Consequently, there is a progressive recovery of the laminate performances at increasing the time duration of the dry phase. In such a context, the flexural fracture surfaces of HW15D$t_d$ and HW30D$t_d$ samples at varying the drying time have to be observed to corroborate these considerations (Figure 9). As the drying time increases, the laminate acquires a progressive stiffening. The local plasticization of the laminae (particularly the inner ones) is gradually reduced. This is evidenced by

the HW15D21 sample (i.e., exposed to salt-fog for 15 days and then stored in dried conditions dried in controlled conditions for 21 days), which shows a fracture morphology quite similar to the unaged specimen. Different remarks must be made by observing the fracture surface of those samples dried after an exposition to salt-fog for 30 days. In this case, the laminate preserves large areas with secondary cracks which propagate transversally to the load direction due to debonding and pull-out of the texture fabrics as well as interlaminar shear fracture.

This experimental evident points out that, as a result of the long exposure to salt-fog environment, the hybrid laminate still preserves a slight weak behavior even after being dried for long time. This suggests that the strengthening contribute due to fiber additions is partially prejudiced. Therefore, the strength loss experienced during the wet phase can be attributed both to reversible and irreversible aging phenomena. On the other hand, the modulus decrease is more probably related to reversible degradative phenomena.

The water absorbed during the wet phase by the epoxy resin used as matrix can be classified as free or bound water [39]. Concerning the former classification, the water molecules can diffuse along the free volume of the matrix, without triggering swelling [46]. Vice versa, the bound water molecules interact with the thermoset matrix through hydrogen bonds, thus weakening the inter-chain hydrogen bonds in addition to promote swelling phenomena [47]. The binding of water molecules with the polar sites of the polymer matrix is usually a process slower than free-volume diffusion, becoming more relevant as more is the duration of the wet phase (i.e., salt-fog exposition) [48]. The free water is characterized by a higher tendency to be lost and gained than the bound water (that required a higher activation energy to be lost due to hydrogen bonding to polar sites), thus affecting the damage sensitivity [22].

In addition to this, further synergistic diffusion mechanisms triggered by capillarity and microcrack transport take place [43]. In particular, the capillarity acts as driving force for the water diffusion toward the matrix bulk and the fiber/matrix interfaces. Water molecules weaken the interfacial strength, thus promoting the fiber-matrix debonding [49]. These phenomena irreversibly affect the

stresses transfer between the fiber and the matrix, thus irreparably reducing the ultimate strength of the laminate. Besides, despite glass fibers show a suitable mechanical stability in humid environments, they could experience a partial reduction of their mechanical performances in wet environment because of local dissolution phenomena on the fiber surface [50].

Finally, it is widely known that flax fibers show a more limited durability in wet environments than glass fibers, due to their hydrophilic nature. This issue plays a key role in the triggering of further damage mechanisms which contribute to the overall worsening of the mechanical response of the hybrid composite. Indeed, water molecules easily interact through hydrogen bonds with polar groups (i.e. hydroxyl terminated groups) of the cellulose molecules within flax fibers [51]. As a consequence, water acts as a plasticizer increasing the molecular mobility as well as the flexibility of the natural fiber [52]. Thus, the cohesive force in the fiber bundle decreases thus leading to reductions both in strength and stiffness. Indeed, the exposition to $Na^+$ and $Cl^-$ ion-rich environment speeds up the degradation mechanisms of the thermoset resin, flax fibers and their interface, due to osmotic diffusion [13].

Furthermore, fiber swelling is promoted by a large water absorption, due to the high susceptibility to moisture absorption of flax fibers [53]. Hence, compression stresses along the radial direction of the fiber/matrix interface are generated. This localized stress state may be sufficient to trigger micro-cracks or local fiber/matrix debonding events [23], thus leading to an irreversible reduction of the failure strength of the composite.

## Conclusion

The issue of the limited durability in humid environments of natural fiber reinforced composites can be overcome through the hybridization of these fibers with synthetic counterparts such as glass fibers. In particular, the presence of outer glass fiber reinforced laminae in the stacking sequence of hybrid composites protects the inner hydrophilic laminae reinforced by flax fibers thus prolonging the material service life.

In such a context, the present paper aims to evaluate the performances reversibility of flax-glass hybrid composites under discontinuous exposition to marine environment. For this purpose, hybrid composites were initially exposed to salt-fog at 35 °C (i.e., wet phase) and then stored at 50% R.H. and 22 °C (i.e., dry phase). The potential recover of the performances of hybrid composites was assessed through three-point bending tests, water uptake analysis and water contact angle measurements carried out at varying the duration of both phases (i.e., wet and dry).

Similar to flax fiber reinforced composites, hybrid composites exhibited both reversible and irreversible degradation phenomena when exposed to salt-fog (i.e., wet phase) besides showing noticeable performances recovery during the dry phase. In particular, the quasi-static mechanical tests evidenced that hybrid composites already exposed to salt-fog up to 30 days, are able to regain more than 98% and about the 90% of their initial stiffness and strength during the dry phase, respectively. Finally, a topological degradation map was developed in order to relate the mechanical performances reduction and recovery of the hybrid laminates with wet and dry phases. It was also possible to evaluate qualitatively both reversible and irreversible degradative contributes highlighting that the strength degradation triggered during salt-fog exposition are closely related to mainly irreversible phenomena whereas the stiffness loss to reversible ones.

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## Figure captions

**Figure 1. Scheme of wet/dry aging phases**

**Figure 2. Water uptake evolution at increasing time during wet (solid line) and dry (dotted line) phases for HW15 (red line) and HW30 (blue line) batches**

**Figure 3. Apparent density and void content evolution of hybrid composites during wet and dry phases**

**Figure 4. Water contact angle (WCA) of hybrid composites during wet and dry phases**

**Figure 5. Stress-strain curves for unaged (i.e., HW0D0) and aged in salt-fog (i.e., HW15D0 and HW30D0) hybrid composites**

**Figure 6. Stress-strain curves at increasing drying time for hybrid composites exposed to salt-fog for a) 15 days (i.e., HW15D$t_d$) and b) 30 days (i.e., HW30D$t_d$). As reference unaged sample (i.e. HW0D0) was added.**

**Figure 7. Percentage variations of (a) flexural strength and (b) modulus of hybrid composites at varying time**

**Figure 8. Strength vs modulus degradation map**

**Figure 9. Three-point bending fractures of hybrid composites at varying time during wet and dry phases**

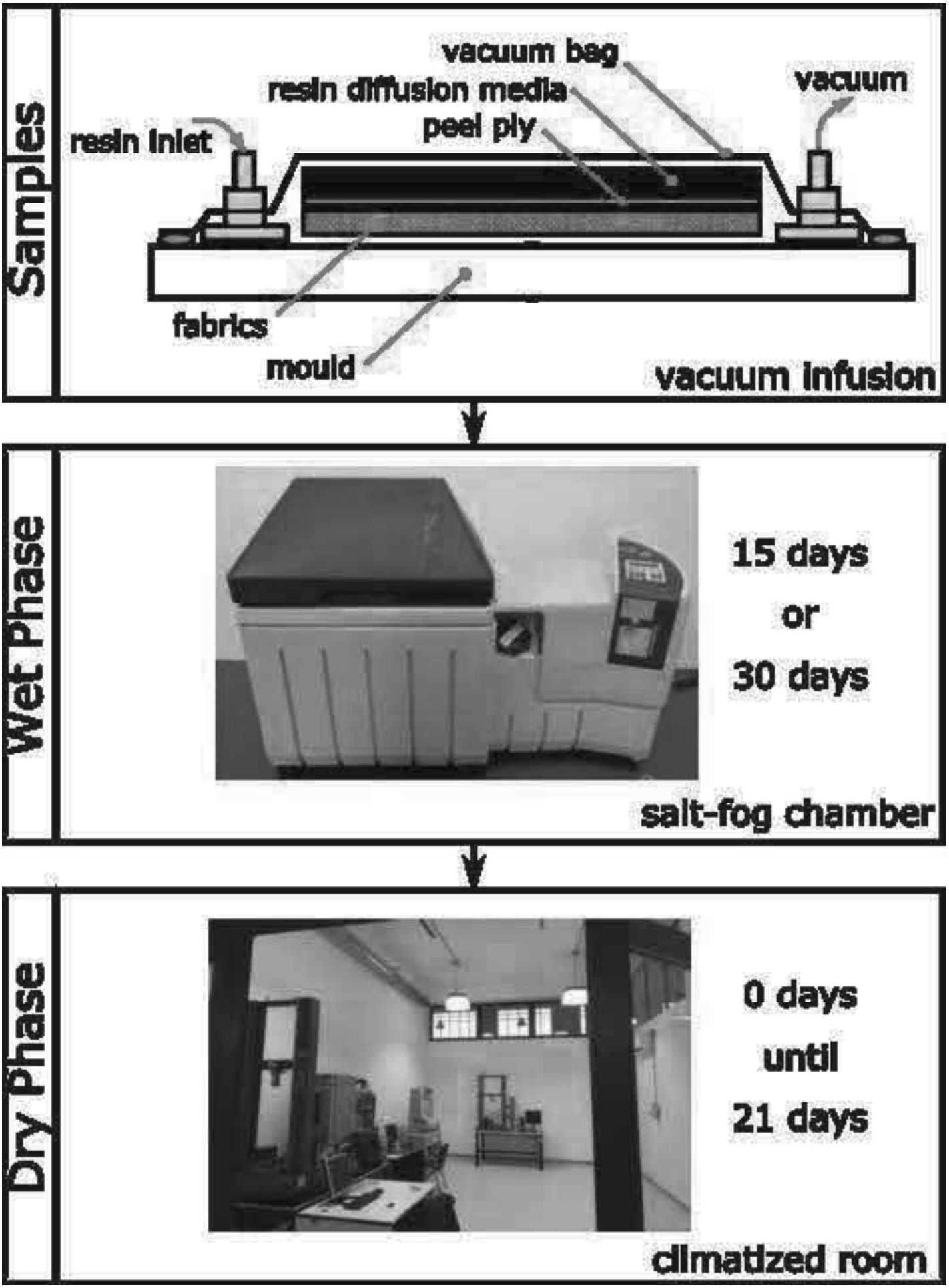
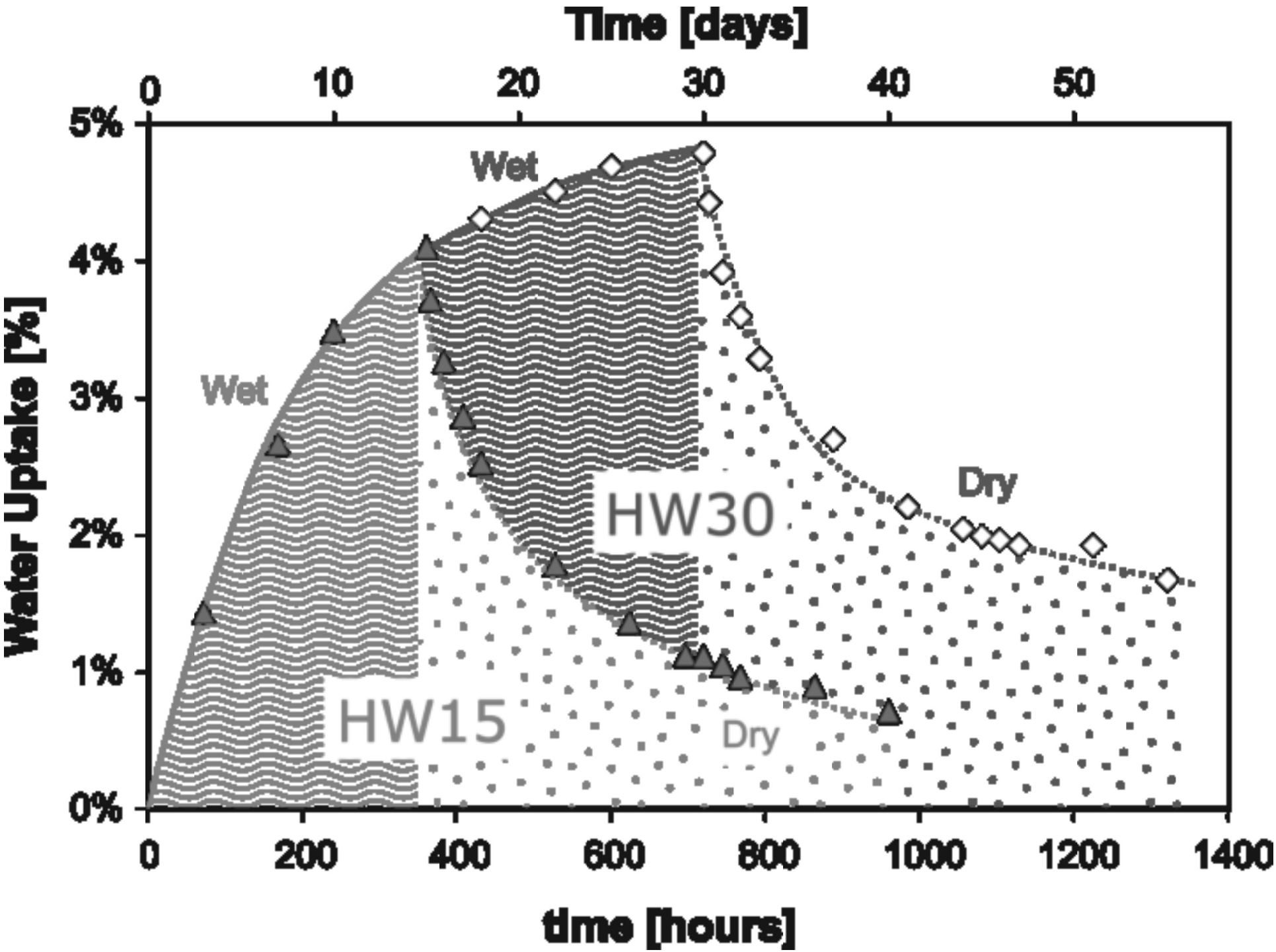
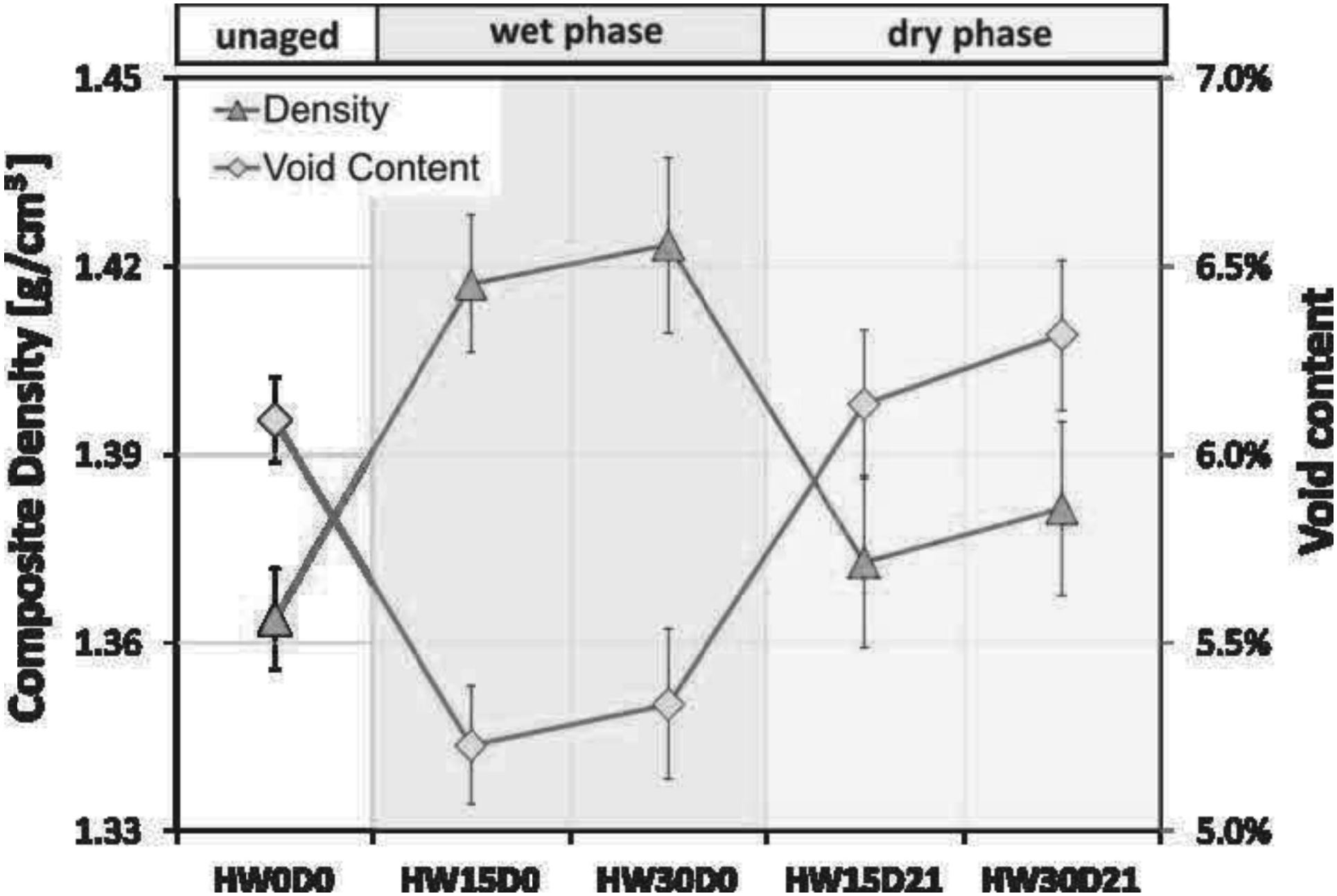
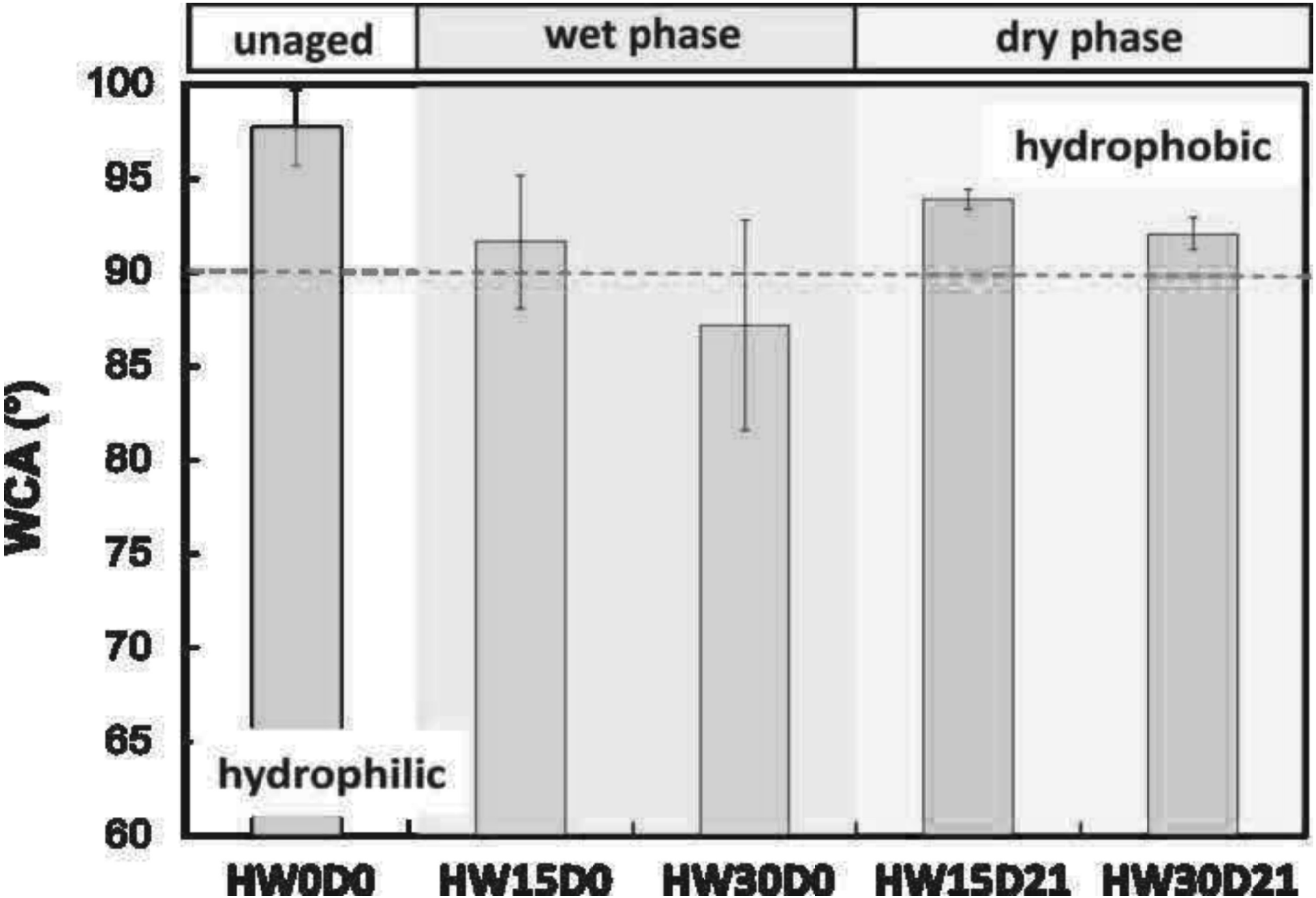

Samples
vacuum bag
resin diffusion media
peel ply
vacuum
resin inlet
fabrics
mould
vacuum infusion
Wet Phase
15 days
or
30 days
salt-fog chamber
Dry Phase
0 days
until
21 days
climatized room

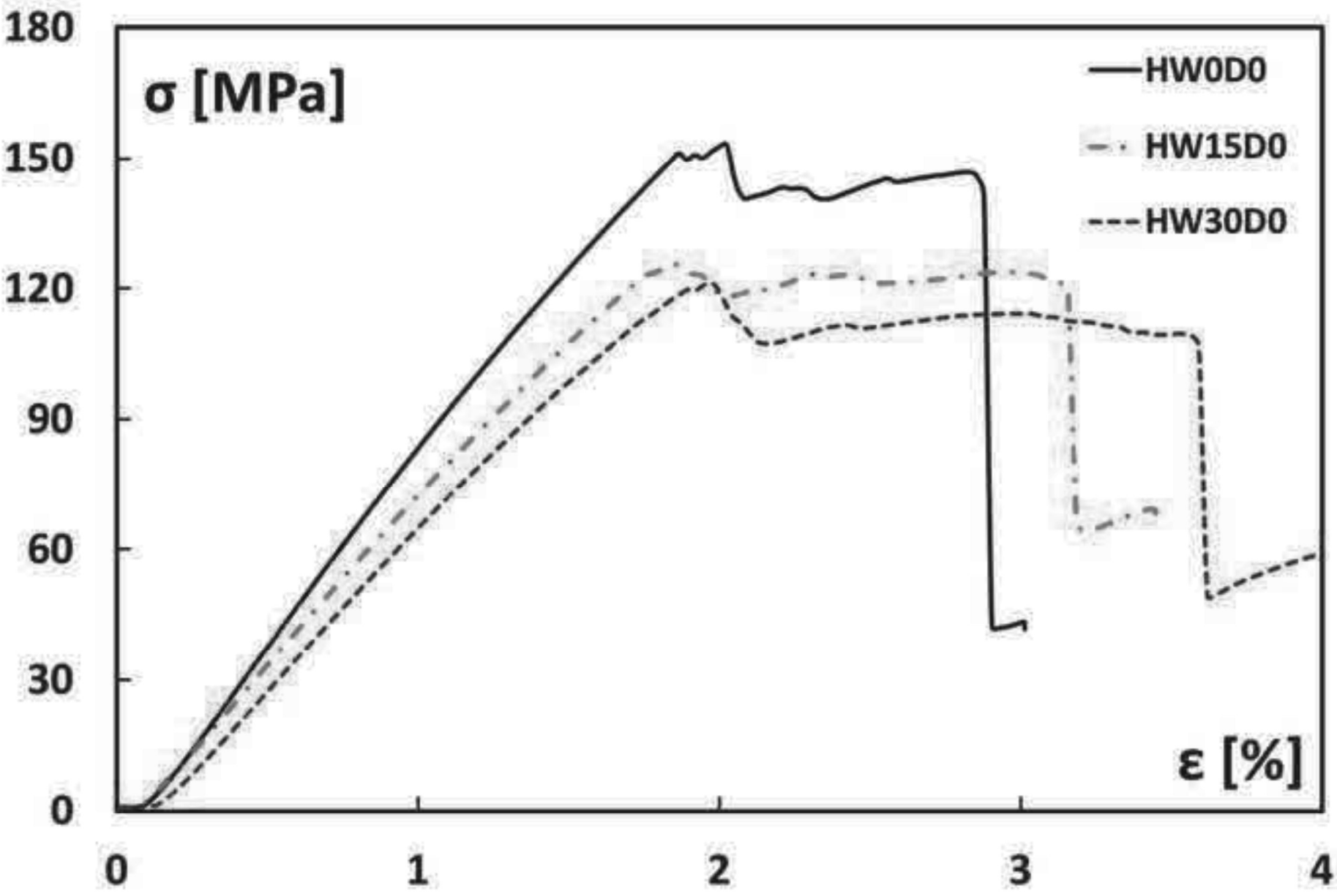
Figure 2

Click here to access/download;Figure;Figure 2.tiff




unaged
wet phase
dry phase
Density
Void Content
1.45
1.42
1.39
1.36
1.33
Composite Density [g/cm³]
7.0%
6.5%
6.0%
5.5%
5.0%
Void content
HW0D0
HW15D0
HW30D0
HW15D21
HW30D21


unaged
wet phase
dry phase
hydrophobic
hydrophilic
WCA (°)
100
95
90
85
80
75
70
65
60
HW0D0
HW15D0
HW30D0
HW15D21
HW30D21


σ [MPa]
HW0D0
HW15D0
HW30D0
ε [%]
180
150
120
90
60
30
0
0
1
2
3
4

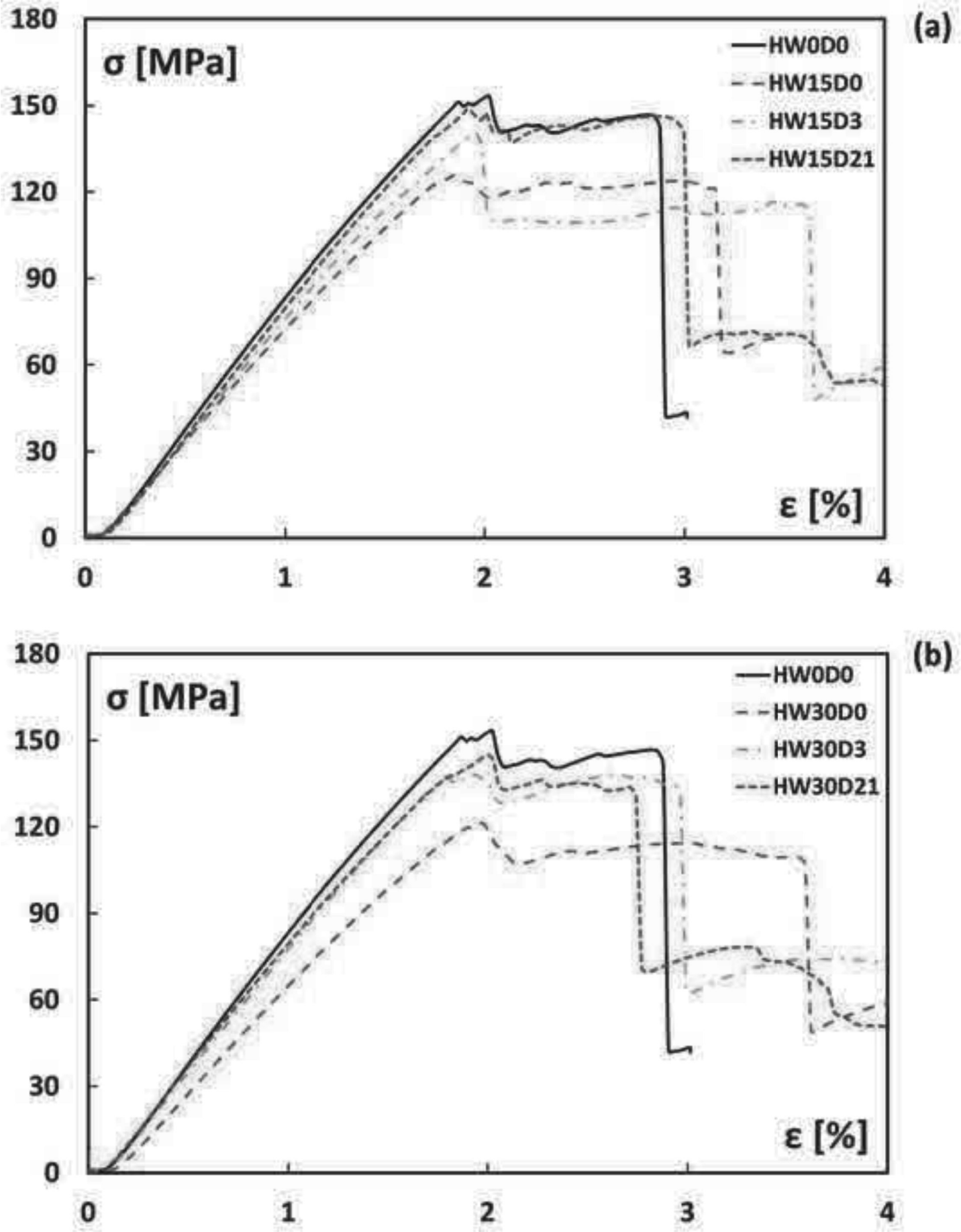
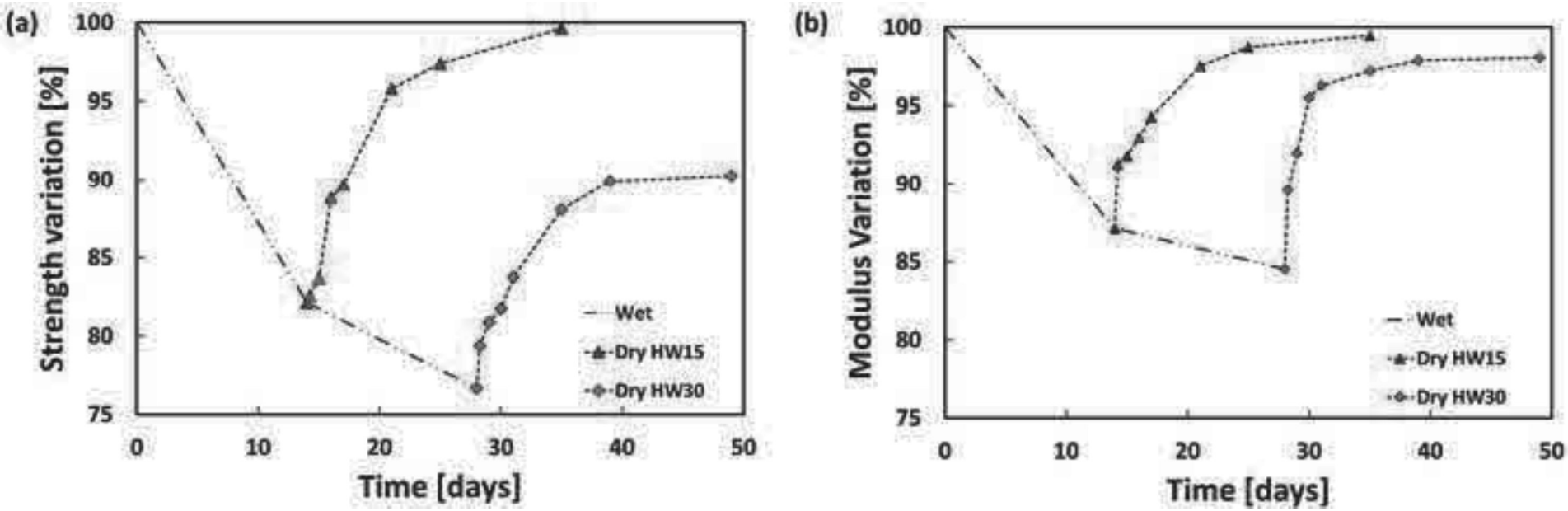
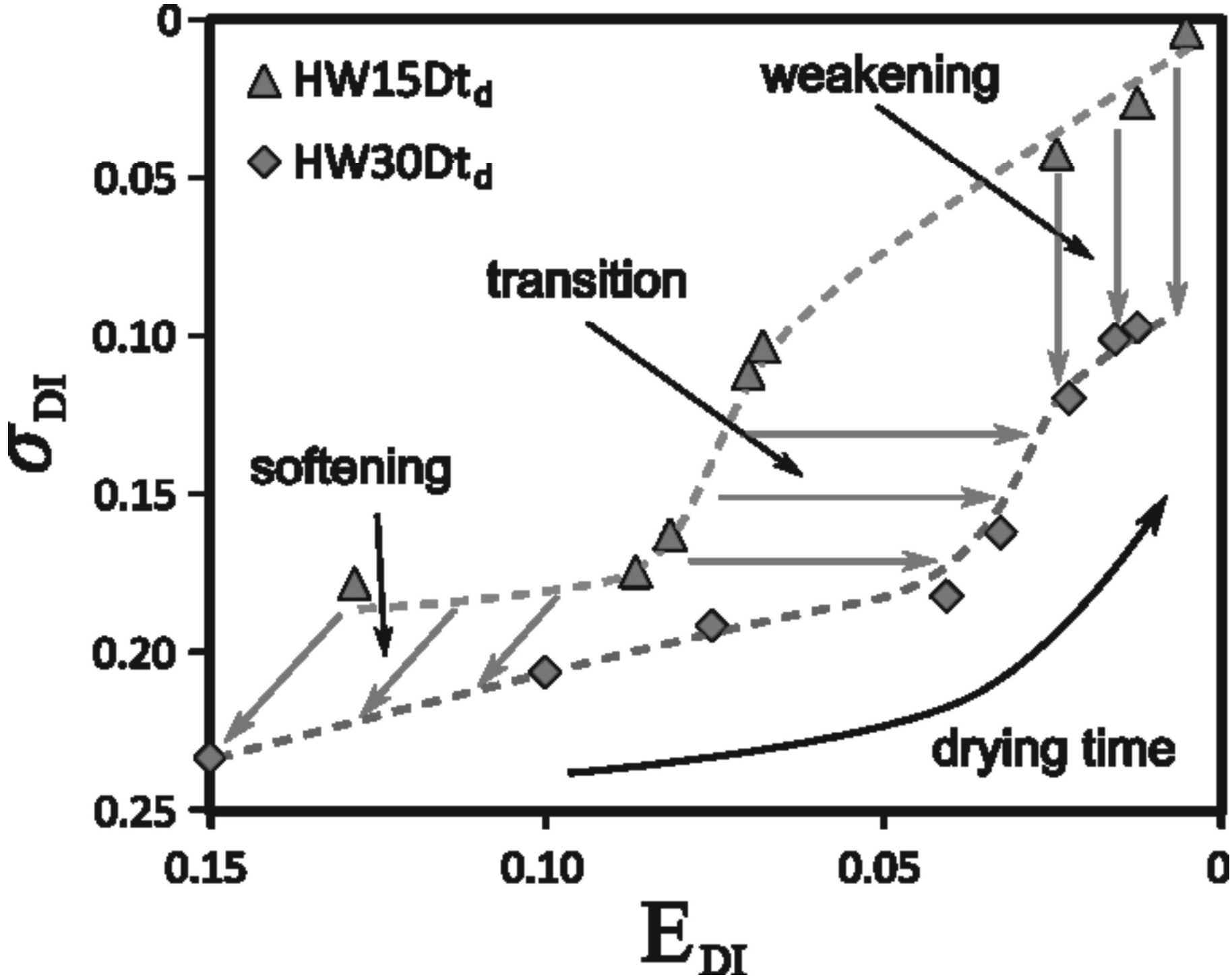
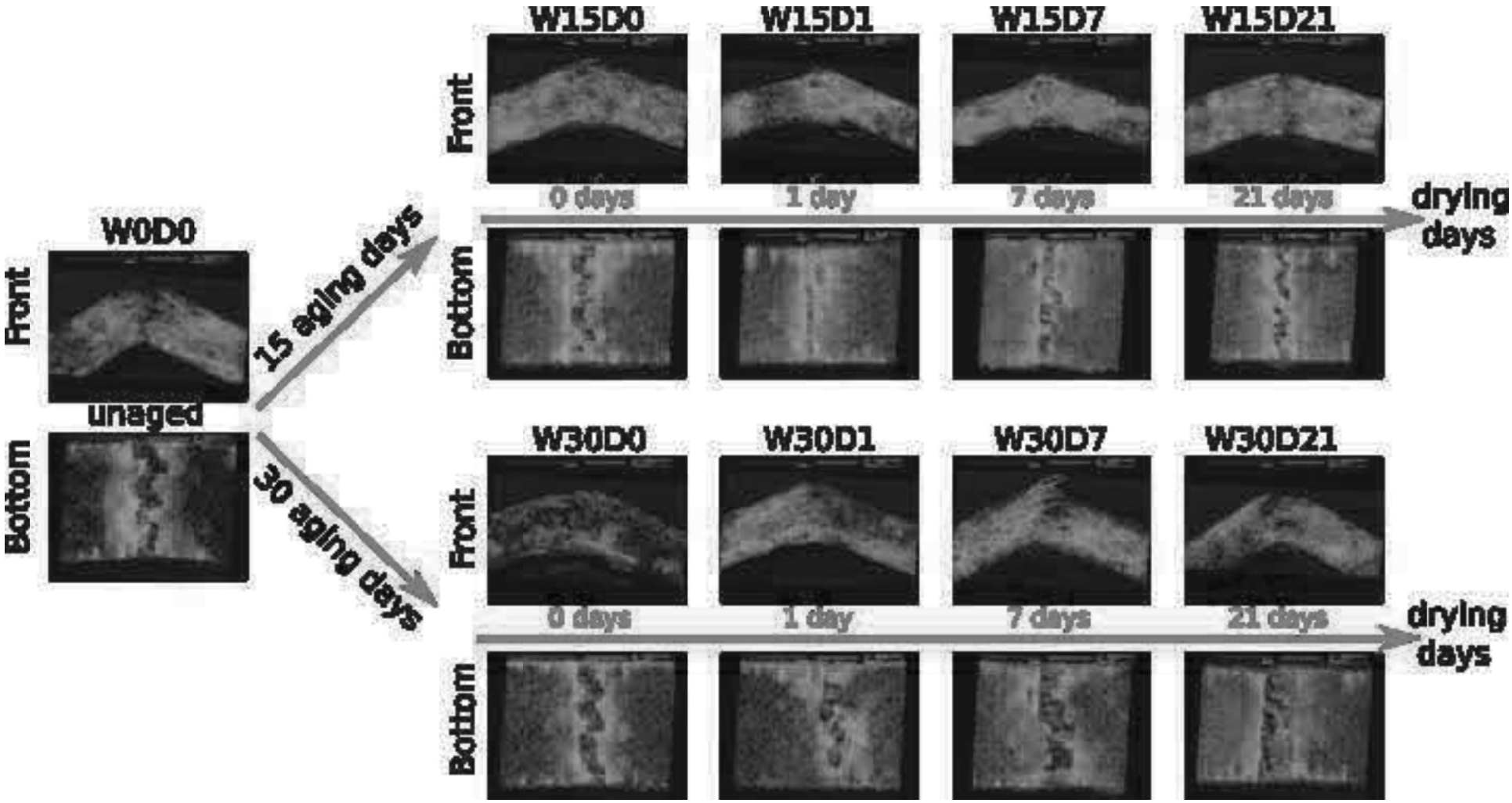

(a)
σ [MPa]
HW0D0
HW15D0
HW15D3
HW15D21
ε [%]
180
150
120
90
60
30
0
0
1
2
3
4
(b)
σ [MPa]
HW0D0
HW30D0
HW30D3
HW30D21
ε [%]
180
150
120
90
60
30
0
0
1
2
3
4

Figure 7






HW15Dt$_d$
HW30Dt$_d$
weakening
transition
softening
drying time
$\sigma_{DI}$
$E_{DI}$
0
0.05
0.10
0.15
0.20
0.25
0.15
0.10
0.05
0


W0D0
Front
Bottom
unaged
15 aging days
30 aging days
W15D0
W15D1
W15D7
W15D21
Front
Bottom
0 days
1 day
7 days
21 days
drying days
W30D0
W30D1
W30D7
W30D21
Front
Bottom
0 days
1 day
7 days
21 days
drying days

**Declaration of interests**

☒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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

V. Fiore, L. Calabrese: Conceptualization, Methodology, Resources, writing - review and editing, Visualization. R. Miranda, D. Badagliacco, C. Sanfilippo: Investigation, Writing - Original Draft. D. Palamara: Investigation, data curation. A. Valenza, E. Proverbio: Supervision, Project administration, Funding acquisition.