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Please submit a plain text version of your cover letter here. If you also wish to upload a file containing your cover letter, please note it here and upload the file when prompted to upload manuscript files. Please note, if you are submitting a revision of your manuscript, there is an opportunity for you to provide your responses to the reviewers later; please do not add them to the cover letter.	06/09/18 Subject: Submission of the paper “Experimental assessment of the improved properties during aging of flax/glass hybrid composite laminates for marine applications” Dear Editor, I would like to submit to your attention the revised version of the manuscript: “Experimental assessment of the improved properties during aging of flax/glass hybrid composite laminates for marine applications” By Luigi Calabrese, Vincenzo Fiore, Tommaso Scalici and Antonino Valenza for a possible publication on “Journal of Applied Polymer Science”. The article was revised in accordance with reviewer comments. I hope you will find the revised paper acceptable for publication in “Journal of Applied Polymer Science”. Best regards, (for the Authors) Luigi Calabrese

Experimental assessment of the improved properties during aging of flax/glass hybrid composite laminates for marine applications

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Abstract

The investigation for natural fibers composites in terms of performance, durability and environmental impact for structural applications in marine environments is a relevant challenge in scientific and industrial field. On this context, the aim of this to assess the durability and mechanical stability in severe environment of epoxy/glass-flax hybrid composites. For the sake of comparison, also full flax and glass epoxy composites were investigated. All samples were exposed to salt-fog environmental conditions up to 60 aging days. Wettability behavior during time was compared with water uptake evolution to assess water sensitivity of hybrid composite configurations. Moreover, quasi-static flexural and dynamic mechanical analysis were carried to evaluate as aging conditions, laminate configuration influence the surface and mechanical performances stability of the hybrid composites. The addition of glass fibers on flax laminate allows to enhance both flexural strength by 90 %, and modulus by 128 %, even if these properties are lower than those of full glass laminates. The results evidenced that the hybridization of flax fibers with glass ones is a practical approach to enhance the aging durability of epoxy/flax composite laminates in marine environmental conditions, obtaining a suitable compromise among environmental impact, mechanical properties, aging resistance and costs.

Keywords: Hybrid composites, Natural fibers, glass fibers, Mechanical properties, durability

1 Introduction

Choosing suitable and effective materials in terms of performance, durability and environmental impact is a stimulating challenging. A special area of interest is the identification of composite structures suitable for marine structural applications. Concerning this last issue, the disposal methods of glass fiber reinforced plastics (GFRPs) and/or their reuse or recycling is a very significant problem for the industrial field [1,2]. In Particular in the nautical sector the issues related to the end of life cycle of fiberglass boats are becoming a relevant aspect for the maintenance, production and design management of the boats itself. In this context, natural fiber compounds can make a valuable contribution to solving the various problems associated with these applications[3,4] by effectively managing also an environmental impact reduction of the product[5,6]. Natural fiber composites are obtaining in the last years a more relevant attention in several industrial applications including automotive, marine, structural and infrastructure[7]. Natural fibers are chosen as reinforcement because they can reduce tool wear during processing, respiratory irritation and as alternatives to artificial fiber composites in the growing global energy crisis and ecological risks[8].

An application limit, however, is represented by the limited mechanical characteristics compared with those of synthetic fibers currently used in the nautical sector[9]. A further issue is the variability of the mechanical performances themselves[10], which imposes high safety coefficients in the design phase as well as more stringent production controls compared to conventional composites manufacturing lay-out.

From this point of view, the production of hybrid composites can represent a valid applied compromise[7,11]. Several experimental studies have shown that the hybridization of natural fibers with GFRPs improves tensile, bending and impact strength of materials[12-14]. Furthermore, the positioning of the glass layers at the extremities in the hybrid laminate stacking sequence allows mechanical strength improvements[9,15]. In particular, Ahmed and Vijayarangan[16] manufactured hybrid glass-jute composites by replacing three external laminae of woven jute mats with glass ones for each side of the laminate, evidencing increases in the tensile strength and modulus of 53% and 30% respectively, when compared to that of only jute laminate.

Based on their wide range of performances design, hybrid natural/glass fiber composites could emerge as a new alternative engineering material in nautical applications, which can optimize the use of GFRP laminates.

A further motivation for the use of hybrid configurations in critical environments such as marine is strictly related to the limited durability of lignocellulosic materials if subjected to physic-chemical attacks[17]. Due to the weak compatibility between hydrophilic natural fibers and hydrophobic thermoset matrices, natural fiber reinforced composites tend to absorb high moisture contents thus leading to rapid decrements of their mechanical performances. On the other hand, it is well known that the mechanical properties decrease of glass/epoxy composites in humid environmental condition becomes stabilized after moisture saturation level[18,19].

In this context, the hybridization of natural fibers with synthetic fibers having superior aging resistance, better thermal and mechanical stability is recently giving a relevant attention thanks to their advantages in terms of compromise between environmental impact, mechanical performances, costs and durability[20-22]. Hybrid composites can support the designer to achieve a better combination of properties than glass fiber reinforced composites. The fibers laminas in a hybrid composite laminate can be combined in several ways leading to variation in their properties [23]. Consequently, a correct design of the hybrid stacking sequence can allow to mitigate the degradation phenomena thus improving the service life of composite components without noticeable increments of environmental impact. Furthermore, hybrid natural/glass composites are receiving the interest by the industrial field (e.g. marine applications) as a compromise solution in reinforced polymer composites, due to its eco-friendly approach and the high performance versus costs ratio that indicate effective and attractive its applicability[24].

Furthermore, the hybridization of lignocellulosic fibers with stronger and more corrosion resistant fibers represents a valid tool in order to improve the moisture resistant behavior of composite structures as well as their durability in severe environment.

Saidane at al.[25] evidenced that the water uptake and the diffusion coefficient are reduced for flax–glass hybridization. In particular, they evidenced that adding glass fiber layers in flax based laminates a positive effect in the Young's modulus and the tensile strength can be observed.

Furthermore, Thwe et al.[26] evidenced that the hybridization of bamboo fibers with glass ones leads to increase of the resistance after water immersion for 3 months at 75°C of polypropylene based composites. The reductions in tensile strength and modulus for bamboo reinforced composites were found to be about twice that of about and glass-bamboo hybrid composites (i.e. 16 and 61%, versus 9 and 29%, respectively). Akil et al. [27] compared the resistance of glass-jute and jute fiber reinforced composites to water immersion and moderate temperature (i.e., up to 80°C), showing that the hybrid system allow to mitigate the effect of both temperature and water on the mechanical properties of the resulting composites. Nevertheless, due to low literature references, further investigations are required concerning the effect of the hybridization with glass fibers on the salt-fog aging resistance of natural fiber reinforced composites.

To this concern, the present study deals with the evaluation of the aging resistance of flax–glass hybrid fiber reinforced composite materials in salt-fog aging environment. Flax, glass and glass-flax composite laminates were manufactured by vacuum infusion process and their performance evolution (such as water uptake, flexural and dynamic mechanical properties) at varying aging time are discussed in detail.

This topic aims to provide reliable information to understand if hybridization can represent an effective solution to mitigate the limits of natural fibers enhancing anyway their advantages. The inherent issues have been addressed in order to evaluate the mechanical performances and to clarify the differences in durability behavior among the three investigated composite laminates batches. The increased durability of hybrid flax–glass composite laminate compared to the flax one is potentially profitable and could represents an important stimulus in order to better develop future scientific activities in order to make reliable these hybrid laminate.

2 Material and methods

2.1 Materials

An epoxy resin SX8 EVO (Mates Italiana s.r.l., Italy) was used as matrix whereas 2x2 twill weave woven flax fabrics with nominal areal weight of 318 g/m^2 (Lineo, France) and plain weave woven glass fabrics with nominal areal weight of 200 g/m^2 (Mike Compositi, Italy) were used as reinforcements.

2.2 Sample preparation

All the composite panels were prepared through vacuum assisted resin infusion method, cured at 25 °C for 24 hours and post-cured at 50 °C for 8 hours. A two stages vacuum pump was used to create maximum vacuum equal to 0.1 atm (absolute). The void volume fraction of the laminates (v_V) was evaluated by comparing their experimental and theoretical densities as following:

$$v_V = \frac{\rho_t - \rho_e}{\rho_e} \tag{1}$$

The experimental density ρ_e was measured using a helium pycnometer Thermo Electron Corporation model Pycnomatic ATC whereas the theoretical density ρ_t was calculated with the following equation:

$$\rho_t = \frac{1}{\left(\frac{W_f}{\rho_f}\right) + \left(\frac{W_m}{\rho_m}\right)} \tag{2}$$

where ρ_m and w_m represent the density and the weight content of epoxy matrix whereas ρ_f and w_f the density and the weight content of fiber.

The stacking sequence, nominal thickness, theoretical and experimental densities (the difference between the experimental density and the theoretical density was used to determine the void volume fraction in the composite laminates) and volume contents (i.e., fiber, matrix and void) of the resulting laminates are reported in Table 1.

CODE	Stacking sequence*	Thickness [mm]	Fiber volume content [%]	ρ_e [g/cm^3]	ρ_t [g/cm^3]	Void content [%]
Glass-Flax	$[G_3/F_3]_s$	5.0 ± 0.12	33.9 ± 2.2	1.307	1.399	6.6 ± 0.4
Glass	$[G]_{16}$	3.0 ± 0.18	39.2 ± 3.1	1.726	1.814	4.8 ± 0.3
Flax	$[F]_{10}$	6.3 ± 0.25	33.4 ± 2.9	1.251	1.268	1.3 ± 0.2

***G = plain weave woven glass fabric; F = twill weave woven flax fabric.**

Table 1: List of manufactured composite laminates

2.3 Salt fog aging test

In order to evaluate the effect of glass fiber hybridization on the durability behavior of flax reinforced epoxy composites, all samples were exposed to salt fog critical environmental, according to ASTM B 117 standard, by using an Angelantoni (Italy) DCTC 600 climatic chamber. The salt fog had a chemical composition of 5% NaCl solution (pH between 6.5 and 7.2) and the temperature of the climatic chamber was 35°C. To assess the composites durability, ten samples for batch were used every 30 days for the mechanical characterization (i.e. quasi-static three point bending and dynamic-mechanical tests) up to 60 days of aging. The removed samples, washed and dried, were stored at room temperature. All samples were tests with 24h in order to ensure no further mechanical decrease evolution or moisture modification during time.

2.4 Weight gain

With the aim of assessing the water uptake versus time evolution, five square samples (100 x 100 mm^2), for each composite laminate, were periodically removed from the climatic chamber within the range 1-60 days, cleaned with a dry cloth (according to ASTM D570), and weighed by using an analytical balance, model AX 224 (Sartorius Italy). The water absorption of the laminates was calculated as weight percentage W according to the expression:

$$W = \frac{W_t - W_0}{W_0} \cdot 100 \quad (\%) \tag{3}$$

Where W_0 and W_t are the initial weight and the weight at aging time t, respectively.

2.5 Wettability tests

Sessile drop contact angle measurements were carried out by using an Attension Theta equipment by Biolin Scientific (Sweden). A 1 µl distilled water droplet was deposited on the laminate surface at room temperature (i.e. 20 °C). The drop was observed by a micro CCD camera (15s recording video) and the image analysis was carried out by a suitable PC software (OneAttension by Biolin Scientific). 10 measurements were performed for each sample. All sessile drop tests were carried out just after water uptake measurements in order to have a better compatibility between water uptake and wettability behavior evolution at increasing aging time for all composite laminates.

2.6 Flexural tests

Three point bending tests were performed according to ASTM D790 standard, using a 5 kN Universal Testing Machine, model Z005 by Zwick/Roell (Germany). Five rectangular samples (width 13 mm and length 115 mm) for unaged and aged batches were tested, setting the span length and the cross-head speed equal to 96 mm and 5.12 mm/min, respectively.

2.7 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical tests were performed, in tensile mode, according to ASTM D 4065 standard, using a dynamic mechanical analyzer model DMA+150 from Metravib (France). Five rectangular samples (width 4 mm and length 46 mm) were tested for each condition from 25°C to 125 °C with heating rate of 5 °C/min in nitrogen atmosphere.

2.8 Scanning Electron Microscopy (SEM) analysis

The analysis of composites morphology was performed on the flexural fractured surfaces by using a scanning electron microscopy model Phenom Pro X by Phenom World (Netherlands) with an accelerating voltage of 10.0 kV. Before analysis, each sample was sputter coated with a thin layer of gold to avoid electrostatic charging under the electron beam.

3 Results and discussion

3.1 Water uptake

The water sorption of all composite samples was calculated according to equation (3). The water uptake percentages at increasing aging time, expressed in days, are reported in Figure 2.

All specimens show a progressive increase in weight gain with increasing aging time in salt fog chamber. In the initial phase there is a significant increase in the water uptake mainly for Flax laminates, which reach an increase more than 5% already after 10 days of salt fog exposition. Subsequently, at longer aging times there is a progressive stabilization of the absorbed water at an equilibrium value for all the compared laminates. In particular, flax laminates evidenced after 60 days of aging the maximum percentage weight gain of 12.6%.

Vice versa, glass laminates showed a quite good weight stability during salt fog exposition, evidencing the lowest water uptake at saturation (i.e., +1.1%) after 60 days. Analogously Assarar et al.[28] evidenced that the water absorption results for the flax–fiber composites is 12 times higher than the glass–fiber composites.

Quite different error bar in the measurements (carried out on five samples) can be evidenced. Flax based laminates evidenced a higher standard deviation in water uptake despite glass one. This difference could mainly imputed to the properties variability of the natural fibers. In fact, lignocellulosic fiber reinforcements can show relevant discrepancies in their mechanical performances[29] since several factors, such as chemical composition, fiber size and density can be affected by local agricultural growing conditions or manufacturing procedures[30,31]. On the other hand, glass-flax hybrid laminates experienced intermediate water uptake at saturation (i.e., 6.9%).

Concerning the water uptake evolution at increasing time in salt fog environment some relevant mechanisms of water absorption in composites laminates can be considered. At first, the diffusion of water through preferential pathways in hydrophilic areas on the resin matrix is favored. Besides, a further mechanism that contribute to water uptake during aging is the capillary water flow into flaws and/or micro-cracks at the fiber/matrix interface. This contribute is significantly influenced by an incomplete wettability or low matrix adhesion to the fiber that stimulates interface debonding [32]. Finally the water transport into the composite laminate is stimulated by micro cracks in the matrix, formed during the manufacturing process or due to aging phenomena [33].

These considerations are confirmed analyzing the SEM images of cross section interfaces on the unaged composite laminates (Figure 3 a,b,c). The flax fabric based laminae are characterized by extensive delaminated areas, as clearly evidenced both in flax and in hybrid laminates (arrows in Figure 3a and Figure 3c) thus favoring water diffusion pathways. This effect is amplified by hydrophilic properties of the natural fiber that favor the resin-matrix interface detachment at increasing aging time. On the contrary, glass laminate (Figure 3b) showed a compact and consistent structure with contiguous glass laminae in the stacking sequence without evident defect or local delaminations. These effects are amplified after 60 aging days, where large delaminated areas are visible in flax-based laminates (Figure3d and Figure 3f), despite glass composite (Figure 3e). It is worth noting that local heterogeneity can be identified in the intersection between warp and weft of fabric. The fabric knot limit the resin wetting to the fiber thus triggering these defects. However, the evident local and non-extended nature of these defects does not affect the water sorption stability at increasing aging time in the salt spray chamber.

If the water uptake behavior follows Fickian diffusion mechanism, it can be expressed by the following formula [34]:

$$\frac{M_t}{M_\infty} = 4\sqrt{\frac{Dt}{\pi h^2}} \tag{4}$$

Where h is the initial sample thickness and M_∞ indicates the water uptake at saturation point. Based on equation 4, at initial stage of the water absorption phenomenon, water uptake at time t (M_t) increases linearly with $t^{0.5}$. Therefore, the average diffusion coefficient (D) can be explicated from equation 4, evaluating the initial slope of the water uptake curves versus square root of time ($k=M_t/M_\infty$), as follows:

$$D = \pi\left(\frac{kh}{4M_\infty}\right)^2 \tag{5}$$

By considering the finite dimensions of the samples the diffusion coefficient needs to be corrected considering the contribute of edges. For rectangular specimen, a corrected diffusion coefficient, D_c, can be determined, hypothesizing that the diffusion rates are the same in all the directions[35,36]:

$$D_c = D\left(1+\frac{h}{L}+\frac{h}{w}\right)^{-2} \tag{6}$$

Where L and w are length and width of the sample, respectively.

In this context, Figure 4 showed the water uptake evolution as function of the square root of time, highlighting the main Fickian parameters according to the equation 2. As can be seen, the water absorption process initially has a linear relationship with time axis for all the specimens. Then, there is a progressive deviation from linearity until reaching a saturation phase at extended salt-fog exposition times. Consequently, compatibly with the water uptake trends shown in Figure 4 for all specimens, the water absorption behavior of all composite batches can be modeled as a Fickian diffusion process.

The slope of the curve, obtained by linear interpolation of data by using qtplot 0.9.8.9-8 software, indicated with k, increases at increasing flax amount in the composite stacking sequence. This behavior can be related to the hydrophilic nature of the flax fibers. These fibers, being lignocellulosic fibers, are mainly constituted by polysaccharides (such as cellulose and hemicellulose) therefore exposed to water fiber swelling and subsequent relevant water uptake is favored[37].

Furthermore, due to this swelling phenomenon, micro-cracks at the fiber/matrix interface or in the brittle epoxy resin matrix may take place, thus involving an additional contribution to the water diffusion through the composite[38]. The water uptake at saturation, after extended aging time, was coded in the plot as M_∞^G, M_∞^{GF} and M_∞^F for glass, glass-flax and flax laminates, respectively. Furthermore, the intersection between linear trend in Fickian area (i.e. low time) and saturation (i.e. longer aging time) identifies the diffusion time, t_D (coded in Figure 4 as t_D^G, t_D^{GF} and t_D^F for glass, glass-flax and flax laminates, respectively).

	k	***M*∞**	***D***	***D*C**	***t*D**
	[1/s^0.5]	***[%]***	***[mm²/s]***	***[mm²/s]***	***[s]***
Glass	$6.86\cdot10^{-6}$	1.1	$0.63\cdot10^{-6}$	$0.56\cdot10^{-6}$	1666
Glass-Flax	$3.46\cdot10^{-5}$	6.8	$1.27\cdot10^{-6}$	$1.05\cdot10^{-6}$	1962
Flax	$6.98\cdot10^{-5}$	12.6	$2.37\cdot10^{-6}$	$1.87\cdot10^{-6}$	1812

Table 2: Water absorption and diffusion coefficients for all composite laminates after aging tests

Water absorption and diffusion coefficients, calculated for the resulting composite laminates after aging exposition are given in Table 2.

The equilibrium water uptake value of glass batch was small and the diffusion coefficient and corrected diffusion coefficient values were $0.63 \cdot 10^{-6}$mm^2/s and $0.56 \cdot 10^{-6}$mm^2/s, respectively. The results reported in table 2 indicates that the absorption performances are proportional to flax fiber content (the glass-flax laminate have water absorption and diffusion coefficient half of flax composite laminate). These considerations are shown on Figure 5 where the water diffusion shielding effect due to glass fiber laminae is schemed.

By assuming such trend, potentially future water sorption parameters could be argued by interpolation approach also for other stacking sequences of glass/flax laminates giving an advance not needing to make experiments for each new combination. The values reported in Figure 2 are in agreement with those reported in the literature[39-41]. Alvarez and Vasquez[40] investigated cyclic water absorption behavior of vinyl-ester and epoxy based glass fiber composites and they observed that the diffusion coefficient increases with temperature. In the present paper, due to the low temperature during salt fog exposition (i.e. 35°C), the fiber–matrix interface presented good adhesion inducing a low water diffusion of glass laminates.

On the other hand, it is worth of noting that by increasing flax fiber amount in the composite stacking sequence a higher diffusion coefficient value can be observed (i.e., glass-flax and flax laminates). These results can be due to the hydrophilic character of natural fibers: consequently, the inclusion of water molecules inside the composite materials was favored at lower aging time as demonstrated by the rate of the diffusion processes[42]. Due to flax fiber swelling internal stresses at the resin/fiber interface are generated favoring debonding or micro-cracking phenomena in the laminate[43]. For these natural fibers, it was shown[44] that moisture is adsorbed in the form of clusters caused by hydroxyl and carboxyl sites in cellulose and hemicellulose. In the case of flax composite batch, the high amount of lignocellulosic fiber contributes to a fast kinetic of water diffusion that will flow towards the composite core through the micro-cracks triggered by the fiber swelling. At the same time, as discussed in the paper of Sen et al.[43], further active diffusion mechanisms, such as capillarity and micro-crack transport, contribute to the diffusion kinetics of water within the composite. In particular, the capillary mechanism involves the flow of water molecules through the bulk of the matrix and along the fiber/matrix interfaces. Water molecules attack the interface, resulting in debonding between fiber and matrix[45]. The result is saturated water uptake values for flax composites one order of magnitude higher than glass fiber composite batch. Analogously a more or less double diffusion coefficient can be shown for the flax composites compared to glass hybridized one confirming the large difference on water sensitivity of this class of composites

3.2 Wettability measurements

Contact angle evolution at varying aging time for glass, flax and glass-flax composites is reported in Figure 6. Sessile drop contact angle measurements have a comparison parameter to roughly show the evolution of hydrophilic/hydrophobic behavior among all investigated composite laminates at increasing aging time. Based on curves trends, it is possible to identify three subsequent stages:

Stage 1: For unaged samples (i.e. 0 aging days) the measured contact angle is only influenced by surface wettability properties of the epoxy resin used as matrix. All batches showed a quite similar contact angle in the range of about 100°-110°. Thus indicates that a mainly hydrophobic behavior can be identified for all composite surfaces, due to the hydrophobic behavior of the thermosetting polymer used as matrix. In particular, flax and glass batches evidenced lowest and highest contact angle, 101.5° and 109.3°, respectively. An intermediate value was observed for glass-flax composite laminate (i.e., 102.5°).

Stage II: At longer aging time, the contact angle slightly decreases. This phenomenon is more evident in flax laminates despite glass ones where a quite constant value can be identified. Two competing phenomena simultaneously occur: the first one consists in the resin post-cure due to the environmental conditions (i.e. temperature 35°C) that exalt the hydrophobic character of the resin[46]. The second one is triggering of germinating damaging phenomena favored by preferential pathways on the resin surface, that could induce the formation of cracks and water permeation, Therefore, this contribute affects the resin permeability and therefore stimulates the water absorption phenomenon. These results indicates that the hydrophilic nature of flax fibers have a relevant role on the water absorption sensitivity in the composites[47]. The high water absorption in flax fibers is due to their micro-structure. In particular, the hydrophilic behavior is an intrinsic characteristic of lignocellulosic flax fibers, which are characterized by a multi-layer structure (i.e. consisting of primary and secondary cell walls) that surrounds a central core, called lumen. Glass fiber composites, instead, evidenced a more stable hydrophobic behavior than flax laminates[48,49].

Moisture causes larger degradation in polymer composites reinforced with lignocellulosic fiber than to synthetic fiber-reinforced composites due the organic nature of the natural fibers. Several papers evidenced the better stability in humid environmental conditions of glass reinforced epoxy composites than flax one: i.e., flax composites absorb much more water than the glass composite [50] thus leading to greater reduction of the mechanical properties.

Therefore, at longer aging time the resin degradation affects the formation of defects[47] that favors water uptake and therefore the reduction of the contact angles (i.e., equal to 73.1°, 82.6° and 96.2° after 25 aging days for flax, glass-flax and glass composites, respectively). Cracks and voids in resin surface induce the water absorption. In fact, the seriously damaged epoxy matrix does not provide a valid shield for the water diffusion that can permeate at the matrix/fiber interface and can be therefore absorbed by the natural fiber itself. This effect is less relevant in glass composite laminates since a higher adhesion to epoxy matrix and better stability in wet environments can be highlighted [51]. This behavior delays in time and reduce in magnitude its contact angle decrease.

STAGE III: Finally at very long aging time, a plateau in the contact angle trends can be identified. This plateau is clearly evident for flax based laminates and can not be identified for full glass laminate. A minimum value was observed for flax laminates (i.e. 67.5°) after about 45 days of salt fog exposition. On the other hand, glass composite laminates evidenced after 60 aging days a contact angle of 79.6°. The activation of stage III is influenced by laminate stacking sequence. In particular, in glass composite laminate it effectively starts later compared to composite laminates reinforced with natural fiber fabrics. This result confirms that the former batch had a less relevant hygroscopic behavior that exalts its wettability performances also at longer aging time, as confirmed by water uptake saturation values observed at very long aging time, according to Figure 2.

The different contact angles found at saturation among the composite laminates is correlated with the greater hydrophilicity of the flax fibers than glass ones. Flax based laminates evidenced significant swelling, despite glass composites where only localized damaged areas, voids or microcracks were observed.

Overall, the wettability behavior of all the resulting composites is in good agreement with their water uptake trends. Although it is worth of noting that the contact angle of glass-flax batch is slightly higher than flax one. Vice versa, the glass-flax batch showed significantly lower water uptake values than the full flax laminate. This trend, observed in Figure 6, can be justified considering that the wettability, being a surface property, is significantly influenced by the presence of flax hydrophilic fibers in the external layers in the stacking sequence and it is dependent on the surface tension. Whereas the water sorption is also dependent on parameters such as voids, cracks, roughness of the composite laminate.

3.3 Flexural tests

Figure 7 shows the quasi-static flexural properties of both unaged and aged laminates. As concerns the unaged samples, obviously glass laminates showed the highest properties among the other ones. In particular, it can be noticed improvements of about 327% and 250% in flexural modulus and strength in comparison to flax laminates, respectively. These differences in the flexural response can be explained taking into account both the lower mechanical properties of flax fibers than glass fibers and the weak adhesion between flax fibers and epoxy matrix (Figure 3)[52]. The hybrid configuration allows to enhance both flexural strength (i.e., +90%) and modulus (i.e., +128%) in comparison to the flax laminate. The enhancement in flexural strength is due to the ability of external glass layers to support bending forces and to guarantee a good stress transfer at the fiber/matrix interface resulting in improved strength properties. On the other hand, the flexural modulus of the glass-flax laminates is improved due to the presence of stiffer glass laminae as external layers in the hybrid configuration. Moreover, even during the entire aging exposition glass laminates maintain higher bending properties than flax ones, whereas the presence of glass laminae as external shield for the weakest flax fibers in hybrid laminates allow to retain intermediate quasi-static mechanical performances. In detail, after 30 days of salt-fog exposition hybrid laminates show about 315% and 96% higher modulus and strength than flax laminates, respectively. At the end of aging campaign, these differences have become equal to about +247% (i.e., flexural modulus) and +110% (i.e., flexural strength).

With the aim to better understand how the mechanical properties of the composite laminates are influenced by the salt fog exposition, the variations of flexural properties at varying the aging time are reported in Figure 8. It is possible to note that flax composites experience greater decrements of both mechanical properties than flax and glass laminates. In comparison to unaged samples, the reduction of flexural modulus of the 60 days aged samples is about 55%, 31% and 6% for flax, glass-flax and glass composites, respectively. Similarly, hybrid laminates experienced intermediate decrease of flexural strength (i.e., -34%) at the end of the aging campaign (i.e. 60 aging days) in comparison to full glass (i.e. -20%) and flax laminates (i.e., -40%).

Analogously Assarar et al.[28] showed that water ageing degrades considerably both stress and elastic modulus of flax fiber composites, with a decrease about 40%. In particular, in accordance with the results showed in Figure 8, they evidenced that the elastic properties of flax fiber composites are hardly affected by water ageing, whereas only the tensile stress have an appreciable decrease in glass fiber composites.

The observed experimental results are in accordance with the water uptake and wettability trends: i.e., the detrimental effects of salt-fog exposition leads to degradation of the hydrophilic flax fibers and the weak interface between these last mentioned and the hydrophobic epoxy matrix interfaces thus explaining the highest reduction in flexural properties experienced by flax composite laminates. Furthermore, voids and cracks within thermoset matrix allow penetration of moisture to the flax fibers. As discussed above, flax fibers consist mainly of hemicellulose and cellulose, both having high tendency to absorb water. For this reason, failure of cellulose and hemicellulose happens during aging exposition thus leading to the weakness of fiber-matrix adhesion. Furthermore, the water molecules can remove the hydrophobic substances of the fiber (e.g. hydrocarbons, waxes and lignin) thus further degrading the fiber-matrix interfacial bonding[53].

Figure 3d-f show SEM images of composite laminates after 60 days of aging. Compared to unaged batches an evident aging on the composite laminate mainly on natural fibers and at fiber/matrix interfaces can be identified. Both chemical and physical degradation phenomena can occur due to ageing exposition. In particular, the chemical degradation is mainly due to the penetration with water molecules inside the composite structure of Na^+ cations and Cl^- anions, thus damaging matrix, fiber and the fiber-matrix interface[41]. On the other hand, the physical degradation consists in the already discussed swelling of flax fibers that degrades their tensile properties, and, consequently, decreases the flexural performance of the composite laminates. The penetration of moisture causes micro-cracking in epoxy matrix and mainly interfacial debonding at the fiber-matrix interface.

The presence of external glass laminae in hybrid laminates shields the internal weaker flax layers, thus allowing lower reduction of flexural properties of glass-flax laminates that, as already stated, represent an effective compromise between full glass and flax laminates.

3.4 Dynamic mechanical analysis

Figure 9 shows the effect of salt-fog exposition on the storage modulus E’ of the resulting laminates. In the unaged condition (Figure 9a), the storage modulus of hybrid laminates (i.e. ~6.4 GPa) is about 32% higher than that of flax laminates (i.e., ~4.3 GPa) but 48% lower than that of glass laminates (i.e., 12.2 GPa) at room temperature (i.e., in the glassy region). These results are in agreement with the quasi-static flexural ones. The SEM images reported in Figure 3, confirm the effective consistence of glass fabric layers despite the flax fabric one, thus involving a better stress transfer on composite laminates characterized by synthetic fabrics as external laminae of the stacking sequence. In this respect, hybrid composite laminates, although characterized by internal flax fabric laminae, are still able to preserve a good structural compactness to guarantee good mechanical stability in the whole temperature range.

Furthermore, considering the mechanical durability of the composite laminates at varying aging time, the storage modulus in the glassy region decreases for all the resulting laminates after 30 days of salt-fog exposition. In particular, glass laminates experienced a slight decrease of the storage modulus in the first 30 days of aging (i.e., from 12.2 GPa to 11.3 GPa) whereas for hybrid and flax laminates these reduction were found to be more evident (i.e., from 6.4 GPa to 4.4 GPa and from 4.3 GPa to 2.5 GPa, respectively). This behavior is mainly due to the progressive damage of the resin surface induced by the formation of cracks thus leading to improve the resin permeability.

As widely discussed in the section 2.5, this phenomenon is more pronounced for hybrid laminates and mainly for flax laminates, which experienced higher weight gain than glass laminates just after 30 days of aging exposition. The presence of hydrophilic fibers in flax or hybrid laminates favors water absorption thus inducing the activation and the propagation of aging phenomena even at short aging times. On the other hand, the presence of the external glass laminae screens the internal flax ones from the above aging phenomena thus lowering the decrease in the storage modulus in the glassy region of the hybrid configuration.

Furthermore, for temperatures higher than glass transition temperature (i.e. in the rubbery region) the storage moduli of all the laminates remain almost constant during the aging exposition.

Figure 10 shows the trends of tanδ as a function of temperature for all the resulting laminates at varying aging exposition. Tanδ (i.e., damping factor), evaluated as the loss modulus to storage modulus ratio, is greatly influenced by the presence of fibers within a polymeric matrix. In particular, the variation of damping factor is mainly due both to shear stress concentrations at the fiber-matrix interfaces and to the viscoelastic energy dissipation within the matrix[54]. Consequently, higher damping can be observed when the fiber-matrix is weak, whereas a better adhesion allows to constrain the polymer chains mobility so that the tanδ is consequently reduced[55].

The tanδ trends for all composite laminates evidence the presence of two peaks, regardless the aging condition. The main peak, centered at about 80°C for all the analyzed cases (see Table 4), can be related to the glass transition of the polymeric matrix. A more or less evident secondary peak appears as a shoulder at higher temperatures (i.e., in the range 100°C -110°C). It can be ascribed to micro mechanical transition due to the presence of an immobilized polymer layer surrounding flax and glass fibers [56]. As stated in our previous paper [48], the tanδ curves of hybrid laminates should evidence two additional peaks (i.e., together with the main one related to the glass transition temperature) due to the polymer layer surrounding the fiber surfaces (glass and flax fiber type). Therefore, in the hybrid configuration analyzed in the present paper, two different interfaces can be identified: i.e., glass/matrix and flax/matrix interfaces. Nevertheless, considering their quite similar interface relaxation temperature (i.e., identifiable by the second peak of the tanδ curves of flax and glass laminates at about 100°C and 104°C, respectively), only a wide and large tanδ peak can be identified in the tanδ curves of hybrid laminates, due to a convolution of both relaxation phenomena.

Dynamic mechanical analysis properties at varying aging time are summarized in Figure 11. As shown in Figure 11a, the glass transition temperature is not influenced neither by the fiber type nor by the aging exposition. In particular, the Tg varies in a narrow range (i.e., 80-83 °C) for all the resulting laminates, regardless the aging condition.

On the other hand, as shown in Figure 11b, the tanδ peak height of unaged flax laminates (i.e., 0.325) is higher than those of glass (i.e., 0.203) and hybrid ones (i.e., 0.251) since fiber-matrix adhesion is weaker for flax fibers than glass fibers, due to the hydrophilic nature of flax fibers and the hydrophobic nature of the epoxy resin used as matrix. Despite the Tg values remain almost constant during the entire aging campaign (regardless both aging condition and fiber type), the tanδ peak height increases as function of the salt-fog exposition time for each laminate: i.e., the mobility of the polymer chains increases due to resin softening favored by water sorption during aging test. Furthermore, it is worth noting by observing Figure 10 it is worth nothing that also the height of the additional and overlapped peaks (i.e., related to micro mechanical transition of polymer layers surrounding flax and glass fibers) increases by increasing the aging exposition, especially for flax laminates. This means that the salt-fog environment worsens the weak interface between the epoxy matrix and the hydrophilic flax fibers more than the stronger one with the hydrophobic glass fiber. Similar results was achieved for hybrid flax-basalt epoxy composites[45].

Overall, the dynamic mechanical characterization confirms the beneficial effect of the hybridization of lignocellulosic fibers (i.e., flax) with synthetic ones (i.e., glass): the presence of the external glass laminae screens the internal flax layers from the aging phenomena thus reducing their decrease on static and dynamic mechanical performances.

Conclusions

Objective of the present paper is the assessment of the effect of glass fiber hybridization on the durability behavior of flax reinforced epoxy composites in order to use glass-flax hybrid composite laminates in marine applications. To this aim, the evolution of water uptake, wettability and mechanical properties (i.e., quasi static and dynamic) of flax, glass and glass-flax laminates exposed to salt-fog environmental conditions for 60 days were evaluated.

The experimental results show that the hydrophilic/hydrophobic behavior of the composites influences their water uptake and wettability, means glass fibers play a noticeable role on the water absorption stability in the composites. Water absorption for the flax–fiber composites is 12 times higher than the glass–fiber composites. Furthermore, the addition of glass fibers on flax laminate allows to enhance both flexural strength by 90 %, and modulus by 128 %, even if these properties are lower than those of full glass laminates. Concerning the aging resistance, it is possible to state that by using external glass laminae one can shield the hydrophilic flax fibers to obtain intermediate quasi-static mechanical performances in the whole campaign, also guarantying about double durability in severe environmental conditions.

Furthermore, the dynamic mechanical analysis confirms the mechanical decrease at increasing aging time for flax based laminates. In particular the storage modulus decreases of about 50% for flax laminates after 60 aging days ascribed both to the hydrophilic nature of flax fibers and to the weak adhesion between flax fiber and epoxy matrix that favor the propagation of aging phenomena. A better dynamic mechanical stability was observed for hybrid composites due to the better glass/resin matrix interfacial adhesion.

These results highlight that the hybridization of lignocellulosic fibers (i.e., flax) with synthetic ones (i.e., glass) allow to obtain composite laminates suitable for marine applications since they represent an effective and suitable compromise in terms of environmental impact, mechanical properties, aging resistance and cost between flax and glass composites. On the basis of these results, future activities will be focused in order to better understand the decrease in mechanical performances on hybrid composites and therefore to assess a durability design approach of these composite materials.

Figure Captions

Figure 1: Scheme of stacking sequence of glass, flax and glass/flax samples

Figure 2: Water uptake evolution at increasing aging time for all composite samples

Figure 3: SEM images of unaged a) flax b) glass c) glass-flax composite laminates and 60 days aged d) flax e) glass f) glass-flax composite laminates

Figure 4: Main diffusion parameters on water uptake evolution at increasing aging time for all composite samples

Figure 5: Scheme of influence of glass fabric laminae on water diffusion for all composite samples

Figure 6: Water contact angle evolution at increasing aging time for all composite samples

Figure 7: Quasi-static flexural properties at varying aging time for all composite samples: a) Strength b) modulus

Figure 8: (a) Flexural strength and (b) modulus retention as function of aging time

Figure 9: Storage modulus versus temperature trends for laminates for (a) 0, (b) 30 and (c) 60 aging days

Figure 10: Tanδ versus temperature trends for laminates for (a) 0, (b) 30 and (c) 60 aging days

Figure 11: Dynamic mechanical analysis properties at varying aging time for laminates Tg a) and Peak height b)

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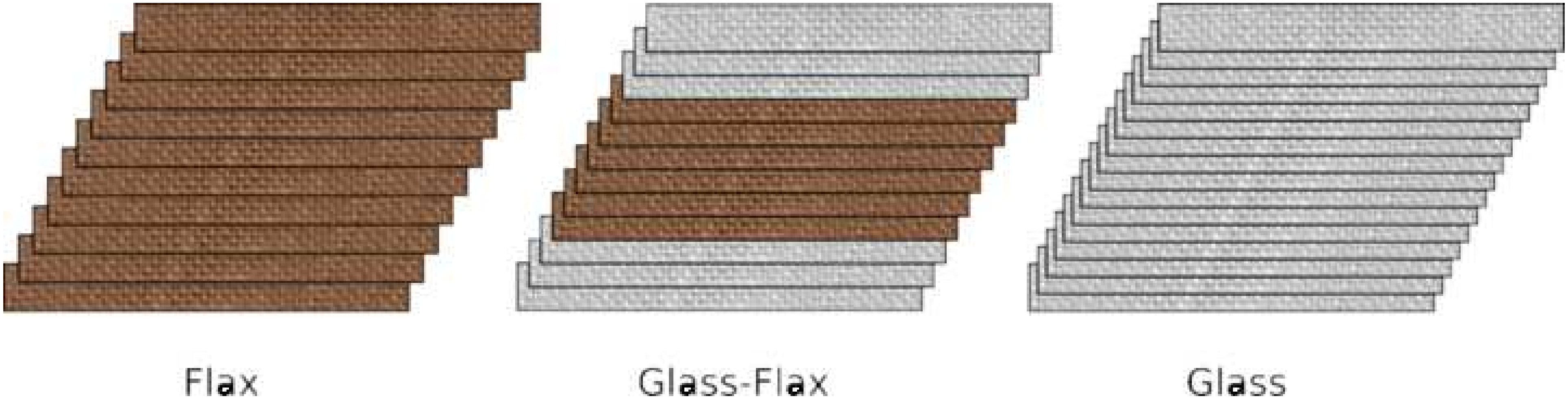
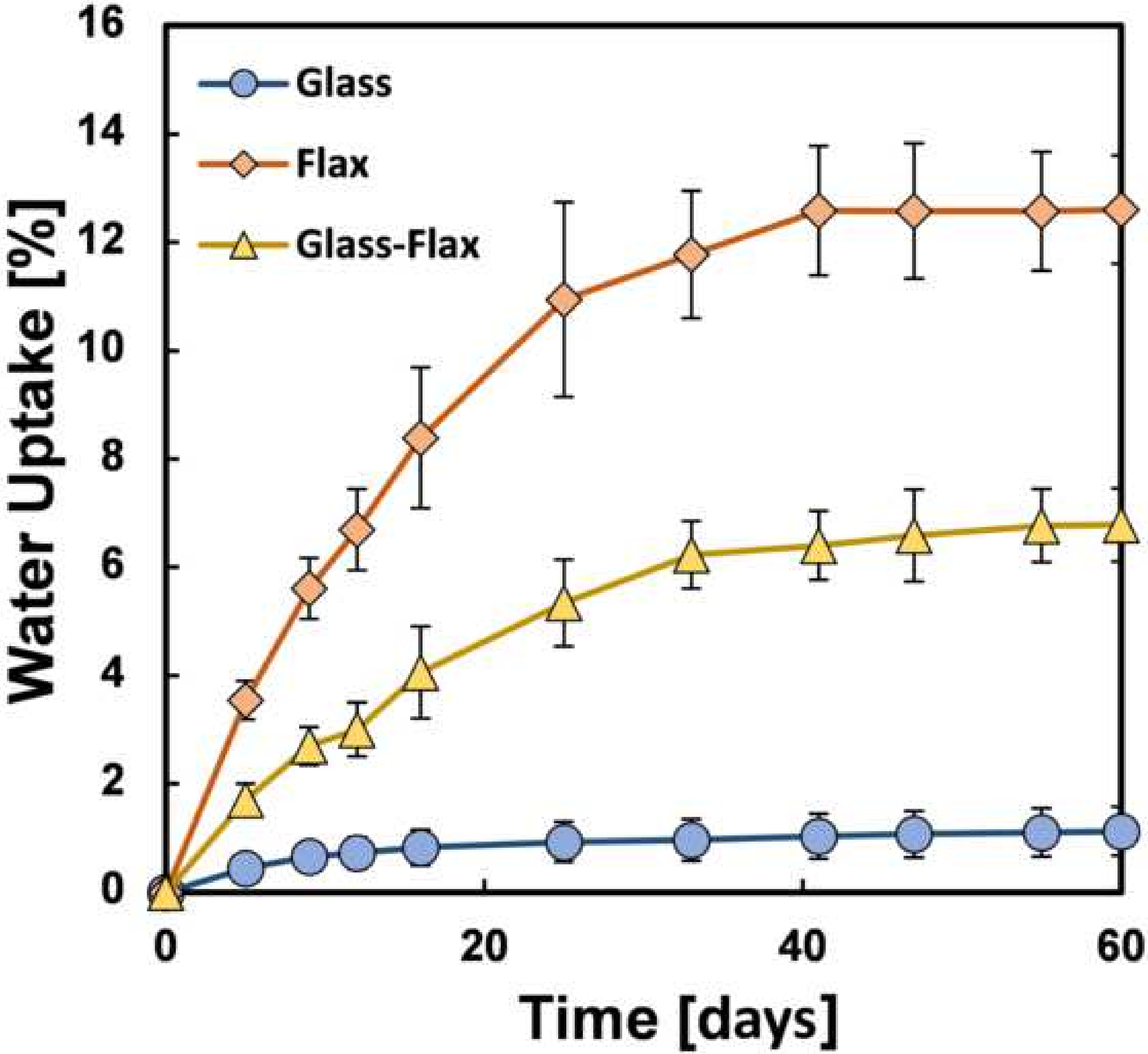
Figure 1

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Flax
Glass-Flax
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8
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4
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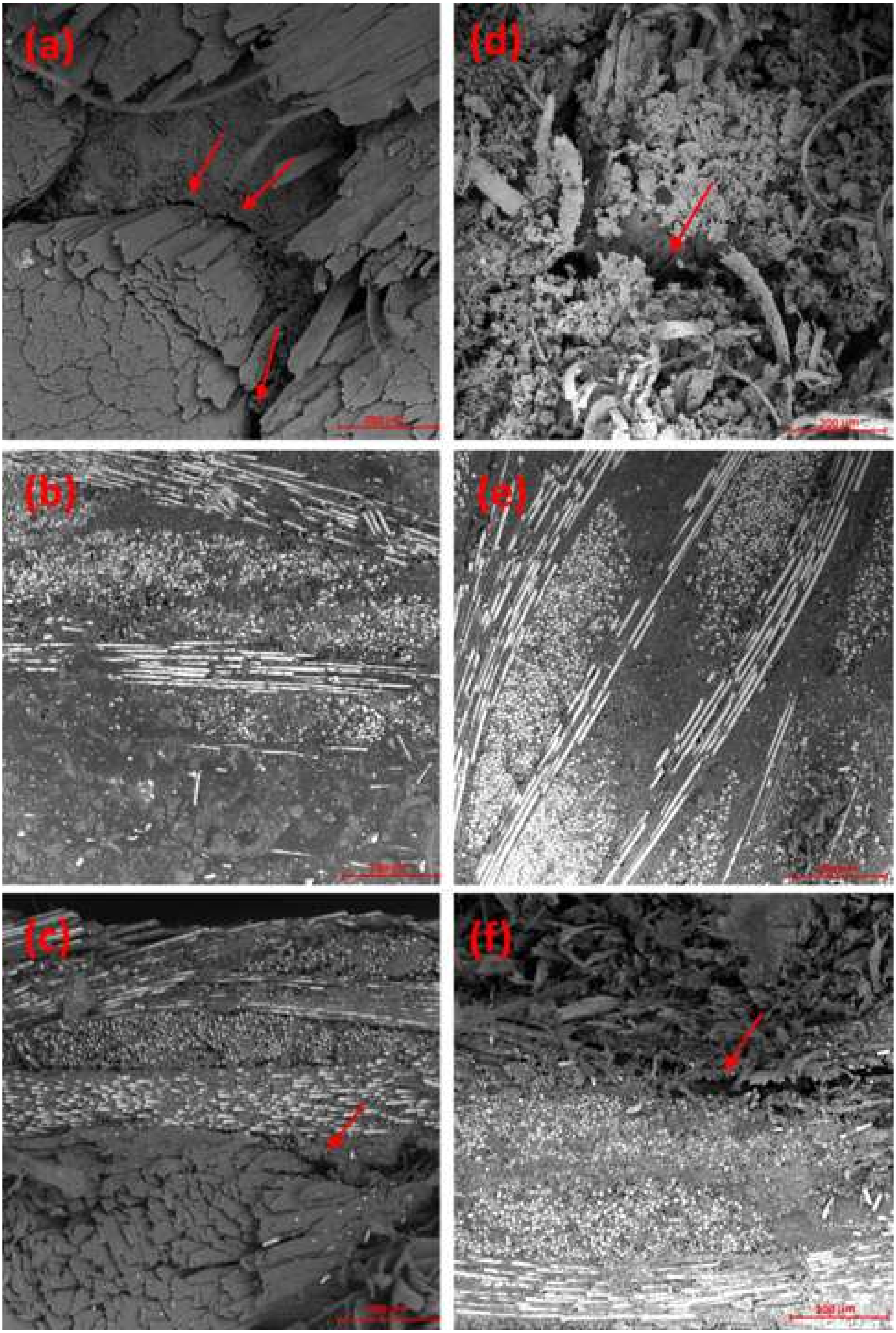
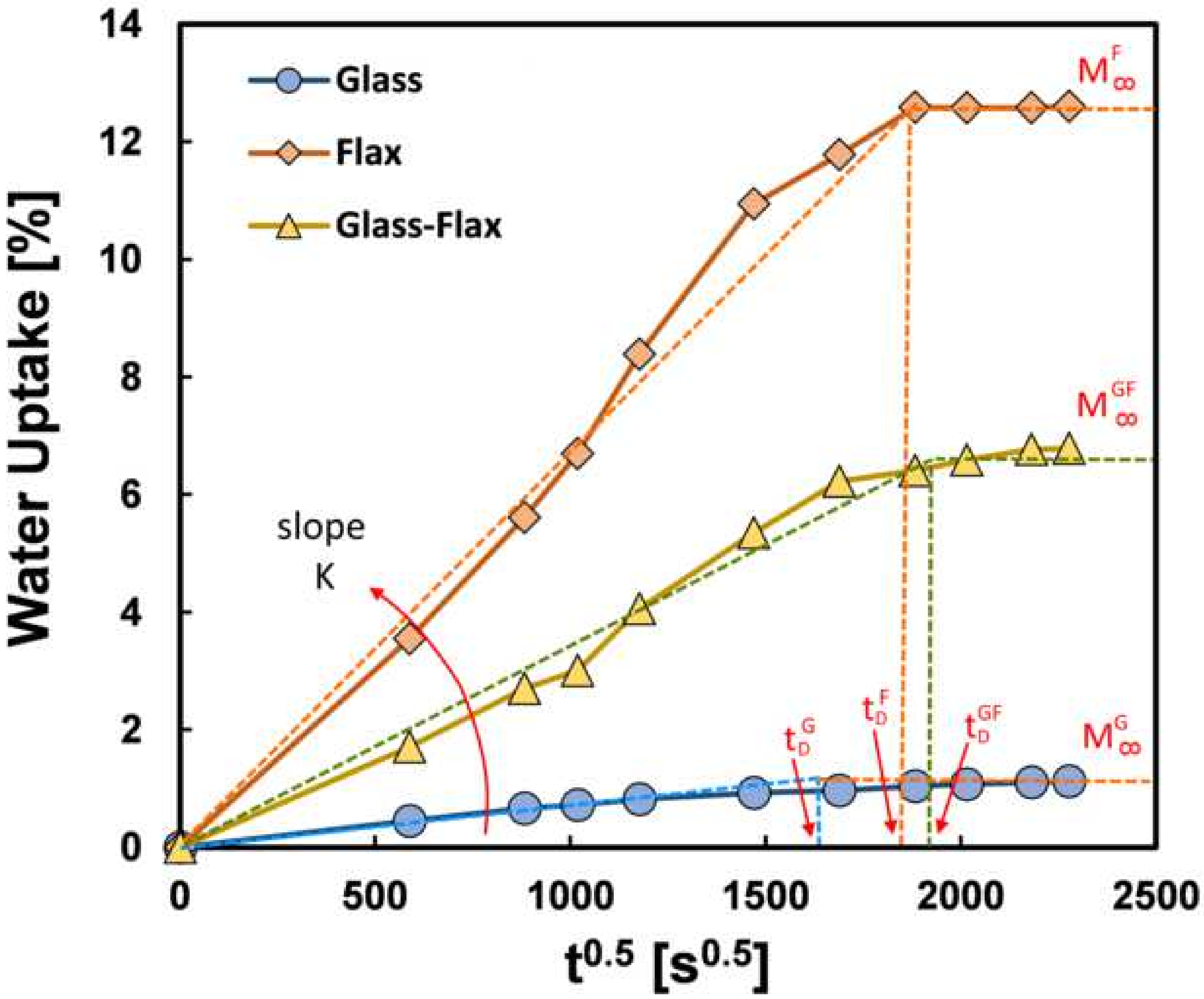
0
20
40
60
Time [days]

Figure 3




Water Uptake [%]
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10
8
6
4
2
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500
1000
1500
2000
2500
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Glass
Flax
Glass-Flax
slope K
M_∞^F
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M_∞^G
t_D^G
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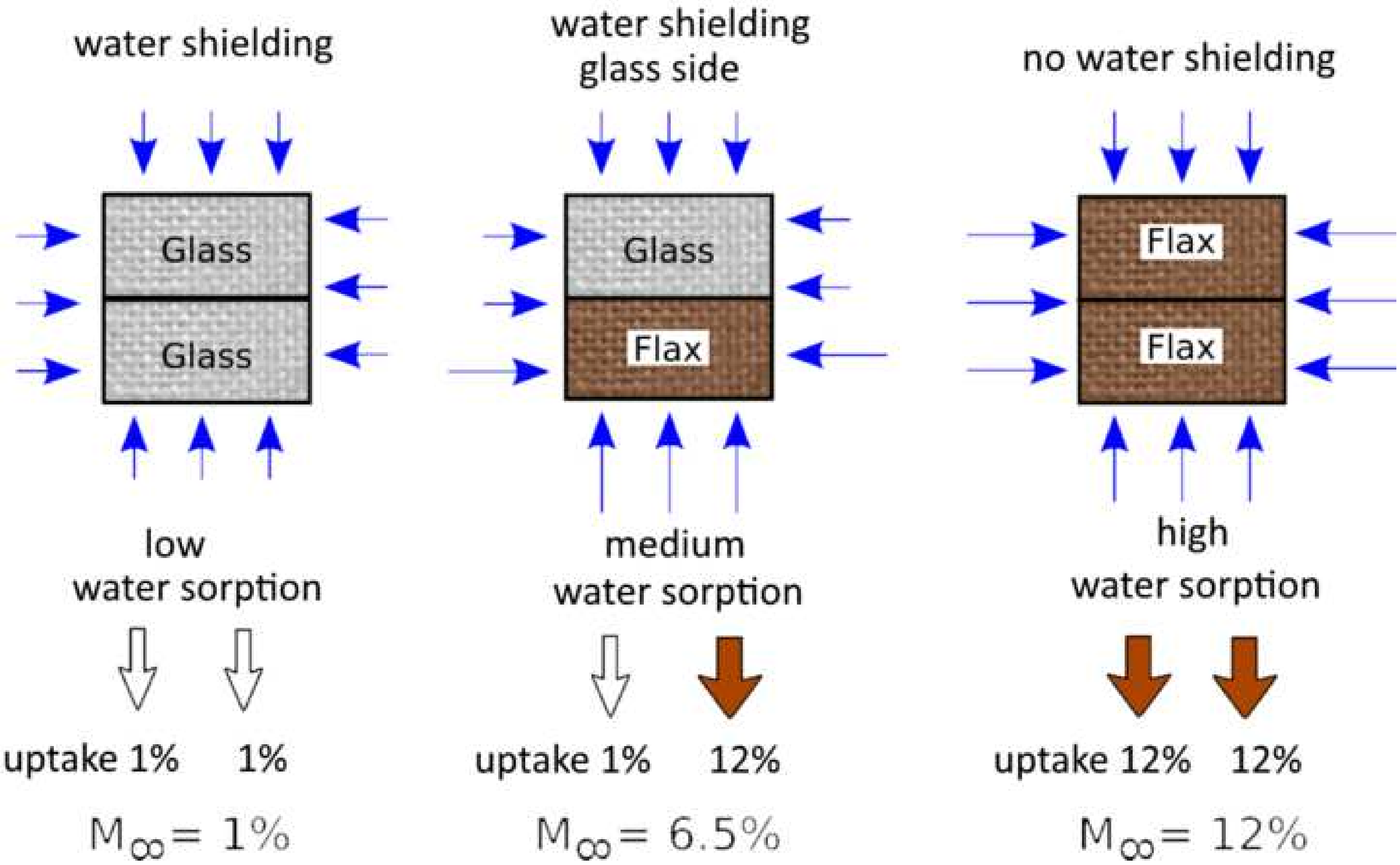
t_D^{GF}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water shielding glass side
no water shielding
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Glass
Glass
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Flax
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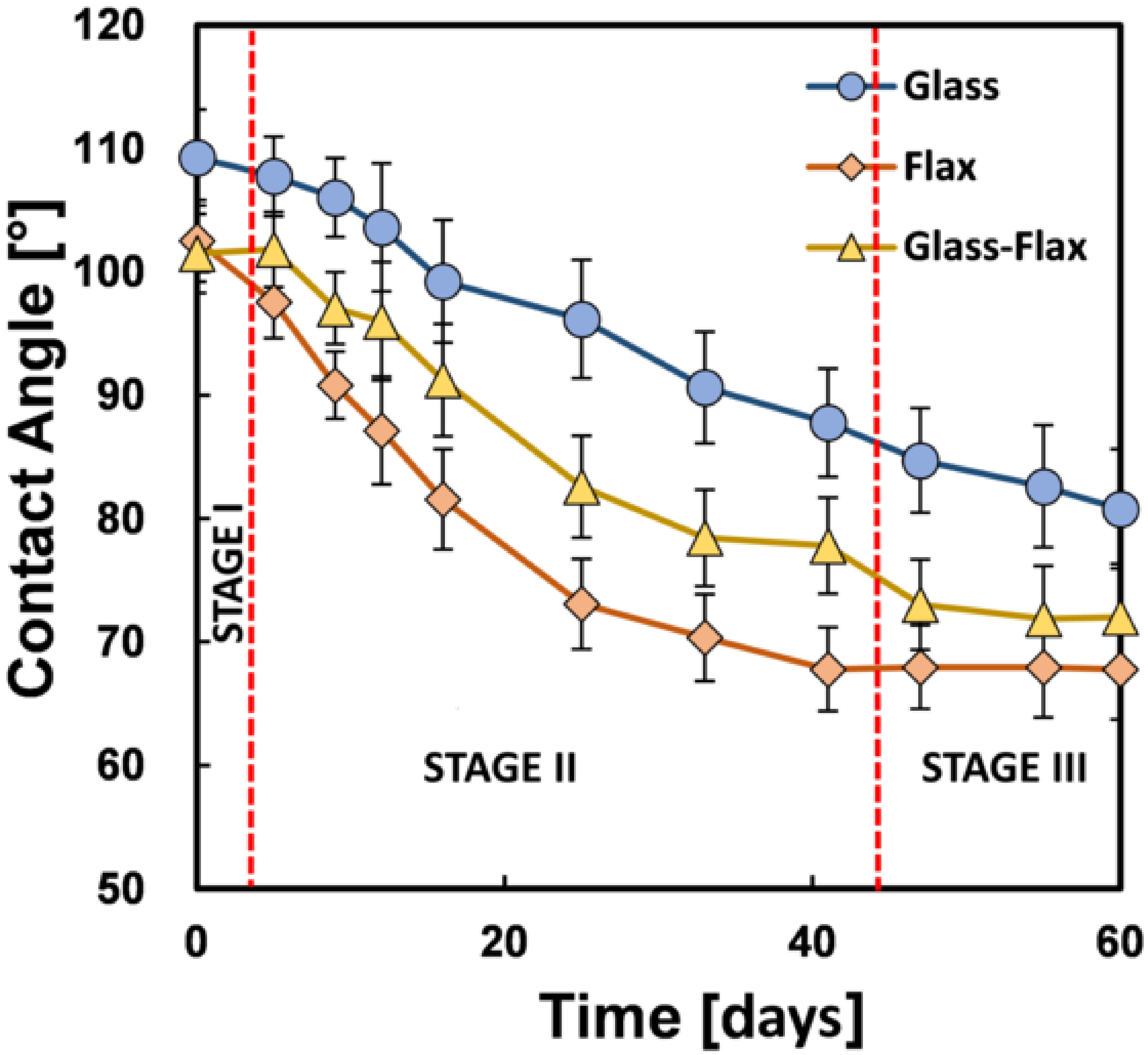
M∞= 1%
M∞= 6.5%
M∞= 12%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Time [days]
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100
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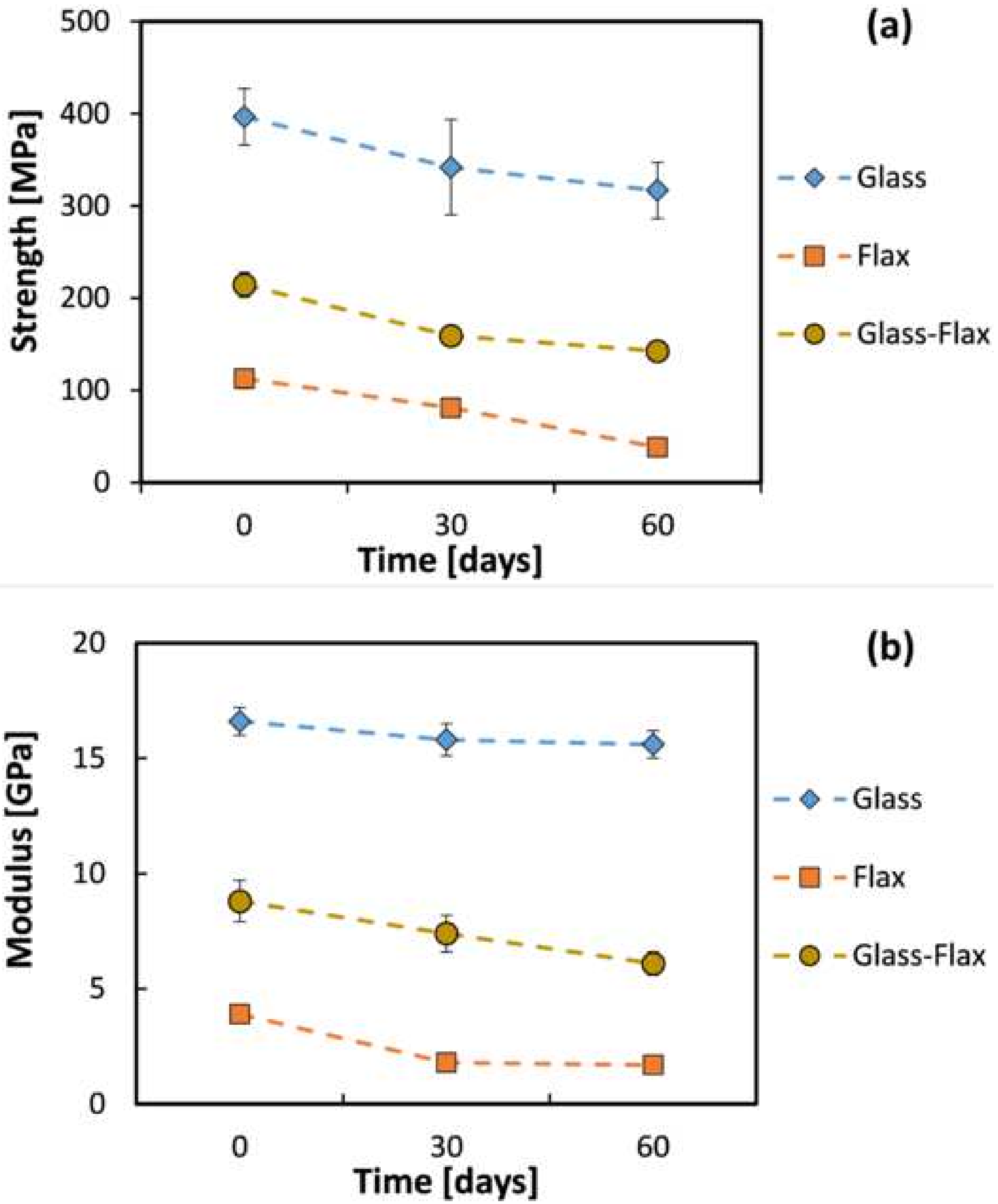
Flax
Glass-Flax
STAGE I
STAGE II
STAGE III

Figure 7


(a)
Strength [MPa]
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30
60
Time [days]
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Flax
Glass-Flax
(b)
Modulus [GPa]
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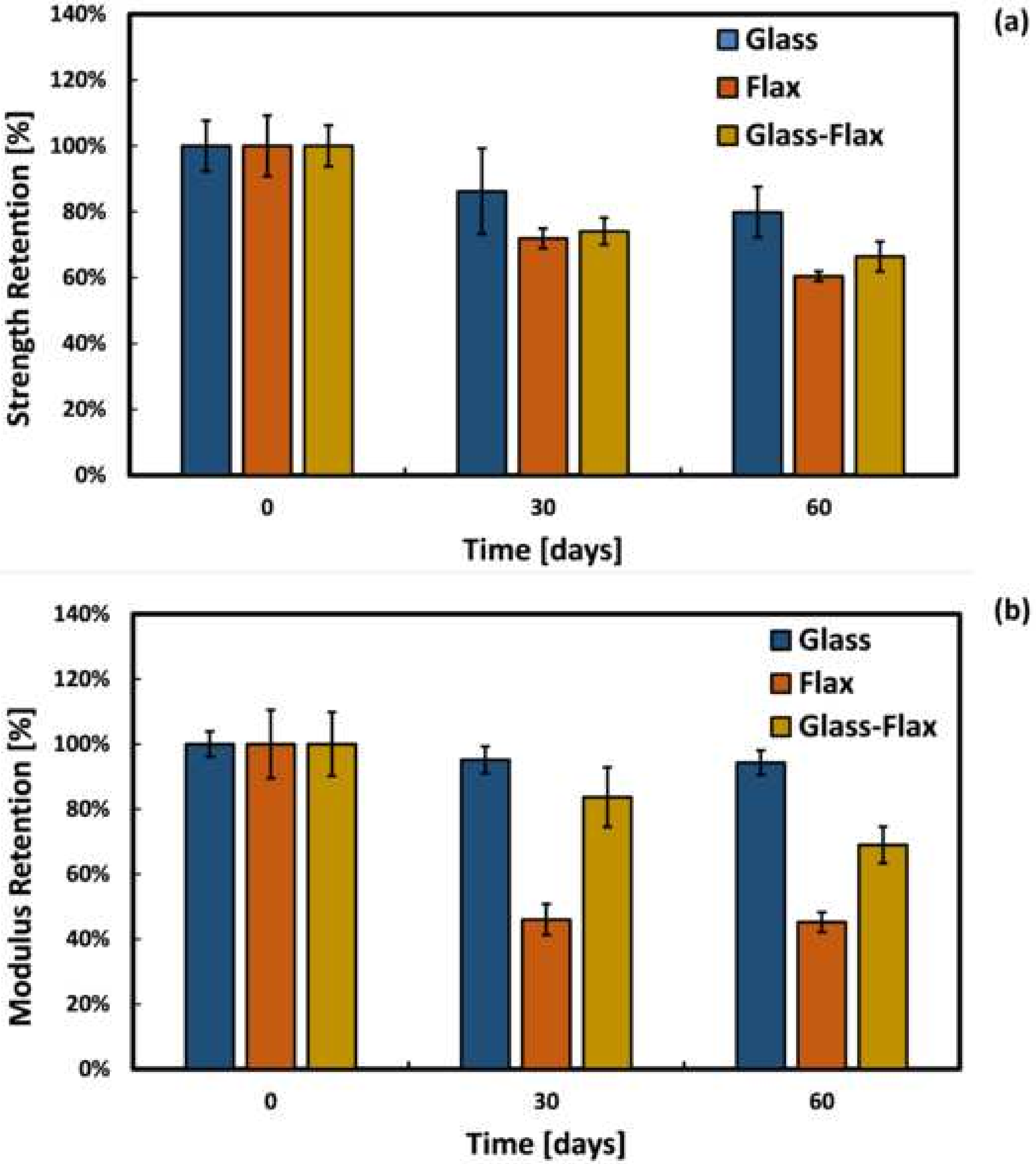
0
0
30
60
Time [days]
Glass
Flax
Glass-Flax

Figure 8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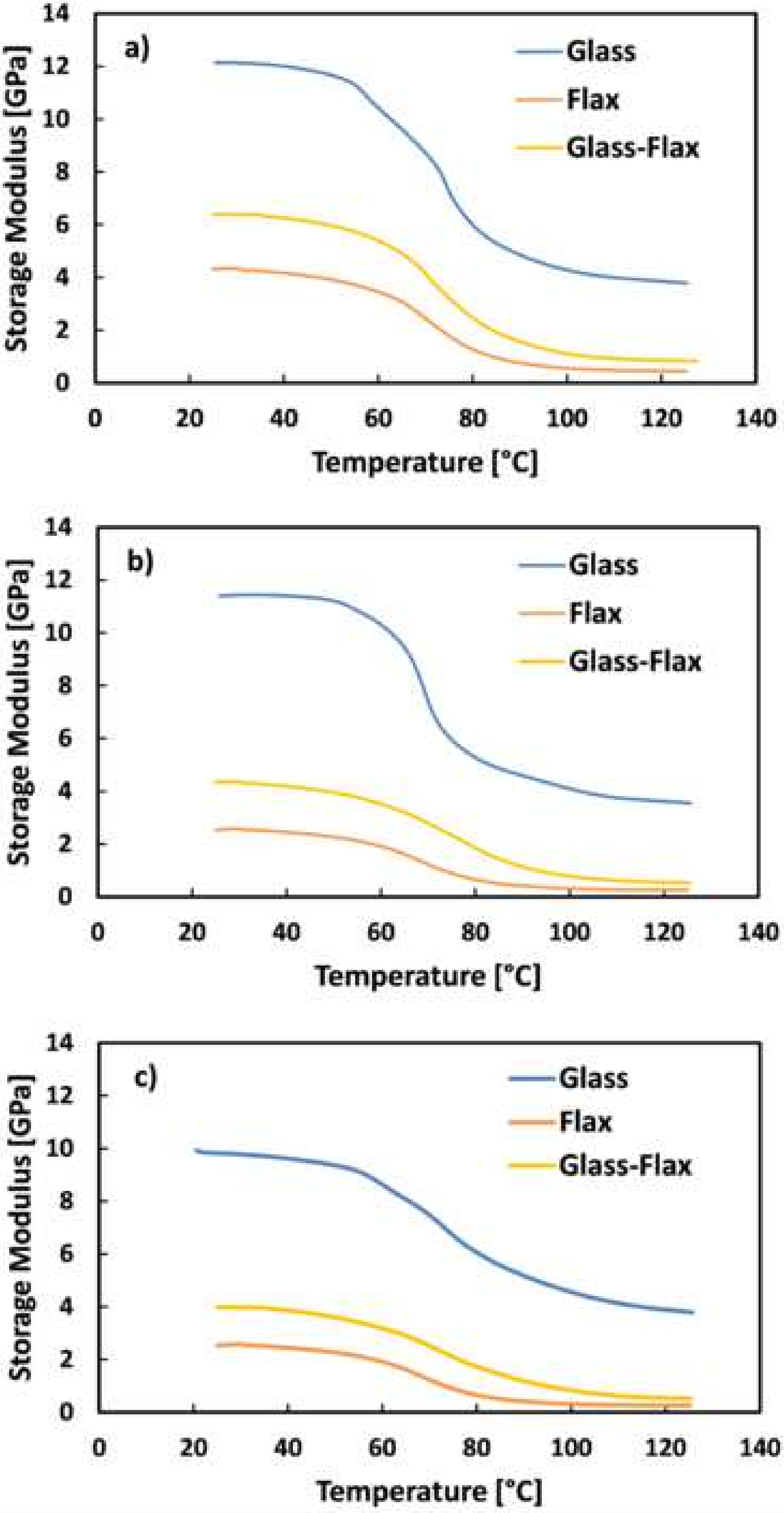
100%
80%
60%
40%
20%
0%
0
30
60
Time [days]
Glass
Flax
Glass-Flax
(b)
Modulus Retention [%]
140%
120%
100%
80%
60%
40%
20%
0%
0
30
60
Time [days]
Glass
Flax
Glass-Flax

Figure 9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Glass
Flax
Glass-Flax
Storage Modulus [GPa]
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4
6
8
10
12
14
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40
60
80
100
120
140
Temperature [°C]
b)
Glass
Flax
Glass-Flax
Storage Modulus [GPa]
0
2
4
6
8
10
12
14
0
20
40
60
80
100
120
140
Temperature [°C]
c)
Glass
Flax
Glass-Flax
Storage Modulus [GPa]
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60
80
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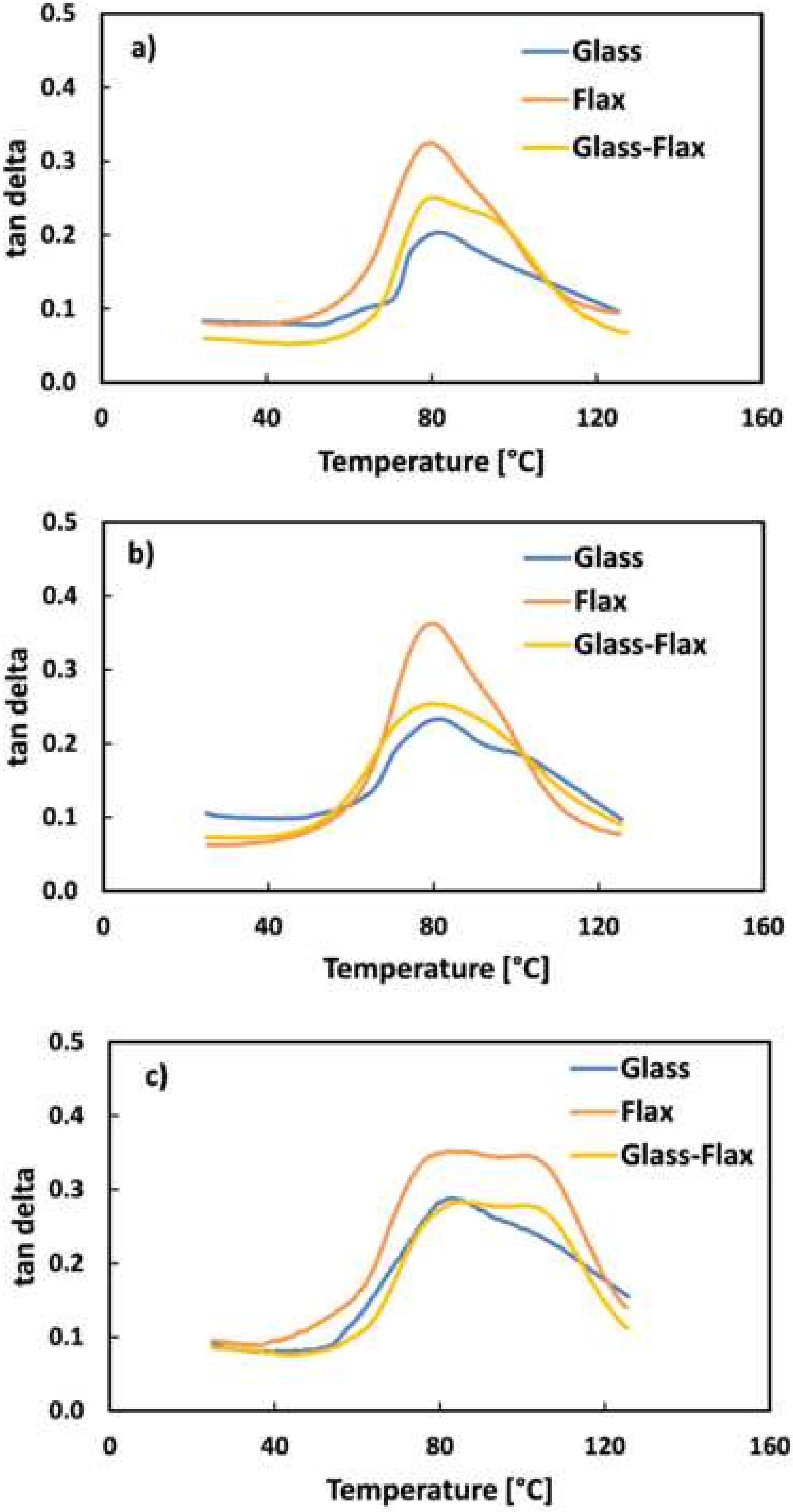
Temperature [°C]

Figure 10


a)
b)
c)
Glass
Flax
Glass-Flax
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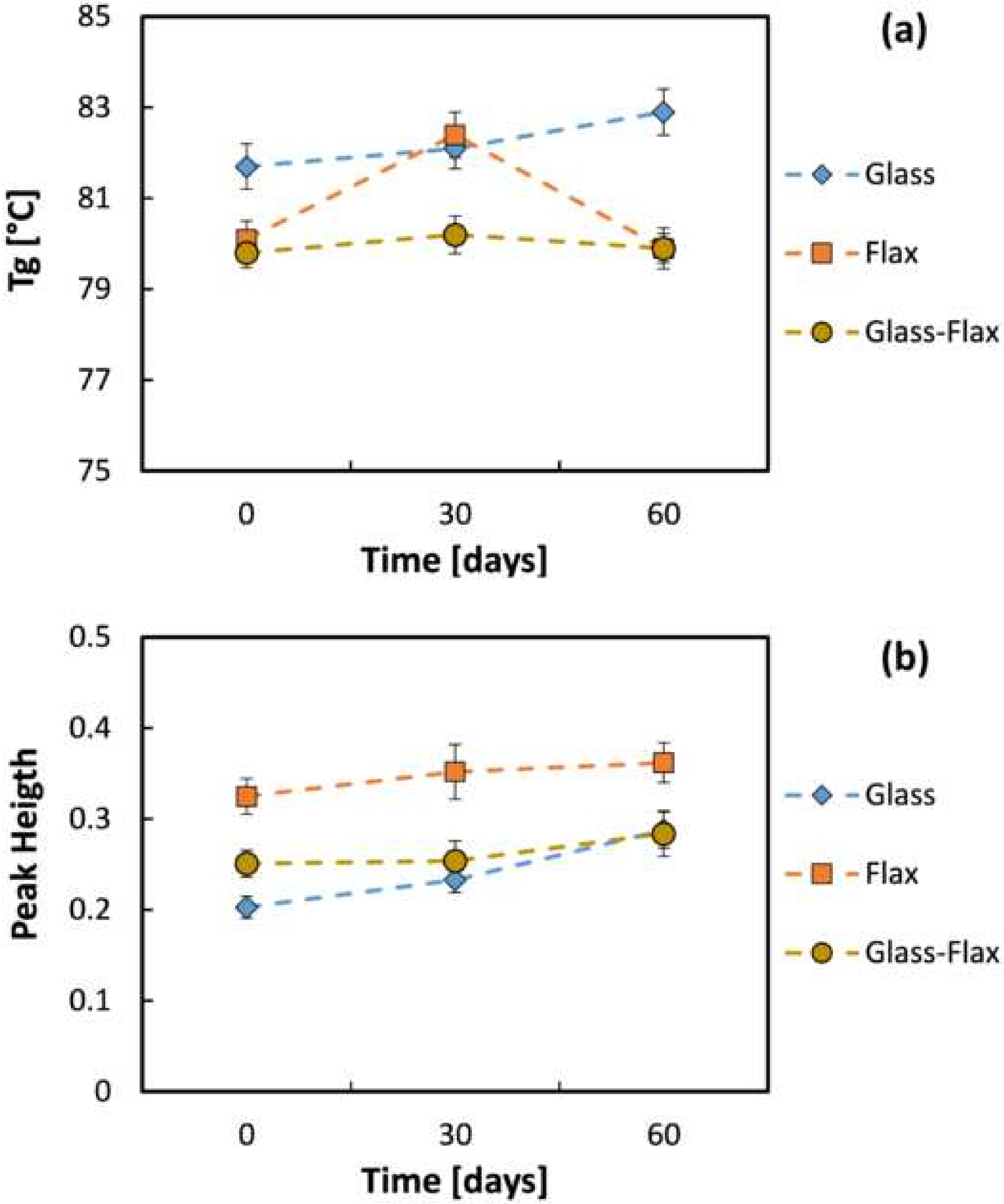
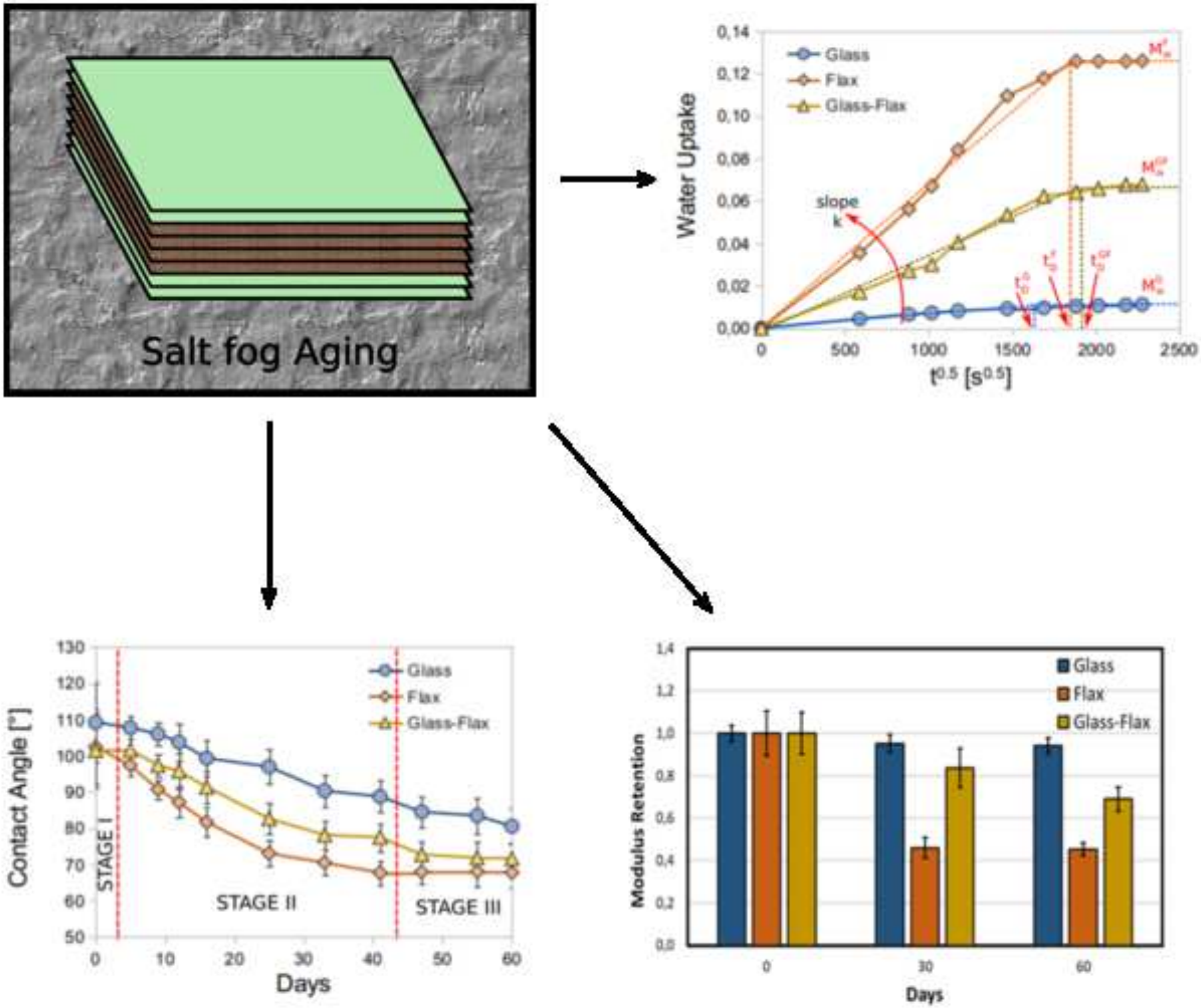
0.5
0
40
80
120
160
Temperature [°C]


(a)
85
83
81
79
77
75
Tg [°C]
0
30
60
Time [days]
Glass
Flax
Glass-Flax
(b)
0.5
0.4
0.3
0.2
0.1
0
Peak Heigth
0
30
60
Time [days]
Glass
Flax
Glass-Flax

Graphical Abstract Image

Hybrid glass-flax composite laminates



Dear Dr. Subramanian Iyer

Executive Editor,

Journal of Applied Polymer Science,

As requested, the Manuscript "Experimental evaluation of the aging behavior of flax/glass hybrid composites for marine applications" has been revised according to the suggestions of the referees that we thank for their invaluable advices.

We have amended the manuscript highlighting in gray, red, blue, green, brown and violet the modifications applied in response to Reviewer #1 #2, #3, #4 #5 and #6 respectively.

We hope that, under this revised form, the paper can be now accepted for publication.

Below, you can find the answers to the referee's queries:

Reviewer #1: **Experimental evaluation of the aging behavior of flax/glass hybrid composites for marine applications**

<u>Page numbers are those from the online pdf document</u>

1. **According to the JAPS account, only Mr. Calabrese is the author, whereas in the manuscript, 3 more persons are mentioned**

A: We apologize for the mistake, the authors of the article are, according to the manuscript: L. Calabrese*, V. Fiore, T. Scalici, A. Valenza

2. **Summary:** The authors produced composites of epoxy resin with (a) glass fibers, (b) flax fibers, and a laminate made of both composites. (To me it is not clear, how exactly the layer stack looked like). The measured different mechanical characteristics and found out, that the flaxglass-laminate showed always intermediate properties, i.e. the respective property was between the one for the flax and the glass composite.

   A: We agree with your considerations. We tried to clearly highlight the layer stack difference among the tested composite laminates adding figure 1.

3. **Title:**
   - 3.1. Does it represent the content?: According to the title, the manuscript is about the experimental evaluation. However, I assume, that the paper should actually be about the (improved?) properties of the composites. Change / rearrange words to make it clearer.
   - 3.2. Moreover you use the word "composite" in the title but "laminates" in the text. This is confusing, as only the glas/fiber material seems to be a laminate. Thus, you do not have a flax/glass composite but a flax / glass laminate.

A: According to the Reviewer's suggestion, the title was rearranges as "Experimental evaluation of the improved properties during aging of flax/glass hybrid composite laminates for marine applications"

4. **Abstract:**
   - 4.1. Length: ok
   - 4.2. Is the context shortly described?: no, please stat shortly, where these coatings are applied in marine environments
   - 4.3. Is the motivation named?: no, this should be included

4.4. Are methods roughly presented?: yes

4.5. Are results roughly presented?: You should mention a few clear results (numbers) in the abstract.

4.6. You do not mention the epoxy resin in the abstract. This indicates, that the material is only made of pure glass and fibers.

A: We apologize for this lack. We revised the abstract adding a short context description and aim of the work. We corrected the abstract also taking into account point 4.5 and 4.6

5. **Introduction:**

5.1. Is the motivation explained?: not clearly enough

5.2. Is the state of the art well reviewed?: In the introduction, a mini-review is given, however not about the questions that are answered in the paper. I am pretty sure, that there are publications, that describe the dependency of mechanical characteristics on added fibers.

Use numbers that are stated in these papers to compare it to your achievements.

A: Following your suggestion the aim of the work was better clarified in the introduction. At the same time, in the revised version an improved state of the art was reported.

6. **Demarcation and novelty**:

6.1. Demarcation is stated: is not decribed in detail, this should definitely be added

6.2. Novelty is given: is not decribed in detail, this should definitely be added

A: The introduction was revised in order to better clarify the novelty of the present work.

7. **Materials and Methods**:

7.1. Is it clear, where the materials come from?: yes

7.2. Is the statistical evaluation described?: no

7.3. Is the description understandable?: to me it is not clear, how the laminates appear. I only can understand, how the composites are made, but I cannot understand the "layer stack".

A: We apologize for this lack. For each testing method we indicated the replicas for batch. Furthermore, in the revised article we added figure 1 where a scheme of the stacking sequence for all composites is reported.

7.4. Check the titles of your method paragraphs. Do you want to describe the method in the title or what you measured? Make it clear.

7.4.1. Salt for aging test <-> sample climatization

7.4.2. Weight gain <-> water uptake

7.4.3. Wettability <-> contact angle evolution / evolution of hydrophilic/hydrophobic behavior

Flexural tests <-> mechanical durability etc. etc.

A: According to Your suggestion, we tried to revise the manuscript in order to homogenize the method paragraphs.

7.5. Please mention the software you used to fit the slopes in Figure 3. Which fitting algorithm did you use?

A: We added software and fitting method used to obtain Figure 3 (Figure 4 in the revised version)

8. **Results and Discussion**:
   The discussion is an explanation, of what happens. But are there also some results, which are not in accordance with yours? Can you compare your numbers with those from other researchers? Be a bit more critical with your results instead of simply saying "it is a good compromise". As the results are not too surprising, you should at least add an in depth interpretation and especially conclusion about your findings.

   A: According to the Reviewer's suggestion, a comparison with literature results and a deeper critical review of results discussion was added in the revised version.

9. **Conclusion**:
   9.1. Is a conclusion drawn?: Only a summary is given, no conclusions are given. What does this mean for the application in marine environment? Can you save money? Can you increase durability? How much?
   9.2. Is and outlook given?: no, this should be included. What are the next steps, what should further be examined?

   A: We slightly modified the conclusion quantifying as possible, the effect of hybridization. Furthermore, some considerations concerning future activities were added.

10. **Language**:
    10.1. Understandable: yes
    10.2. Grammar: should be checked by a native speaker
    10.3. Set points, commas etc: ok

    A: We revised the manuscript trying to improve the English.
11. **Sources**:
    11.1. **Amount**: good
    11.2. **Correctness**:
        11.2.1. No obvious errors found
    11.3. **Currentness of sources**:
        11.3.1. 2~ sources cited from before 2000
        11.3.2. 16~ sources from 2001-2010
        11.3.3. 21~ sources from 2011-2015
        11.3.4. 16~ source from 2016-2018

        → very good

    11.4. **Output style**: please adapt the reference style and output style to the journal's requirements.

    A: A Mendeley csl file was used to use the correct reference style. Furthermore, for each reference the identifying doi code was reported.

12. **Highlights:**
    12.1. Not given. Please check, if the journal requires it.

    A: We checked it. The Author Guidelines not evidenced the request of highlights
13. **Graphical abstract**: check, if this images are readable when the whole abstract is presented in smaller size on the JAPS website.

A: We checked that the graphical abstract is 300 dpi.

14. Figures and Tables:

14.1. Are the formats uniform?: no, this should be changed. Same colors, same frames, same typesetting.

A: Following your suggestion, figures were rearranged where possible.

14.2. Adapt the label style to the journals requirements

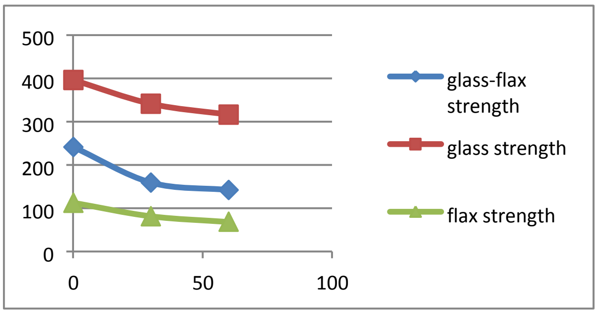
A: We modified the tables according to journal style requirements

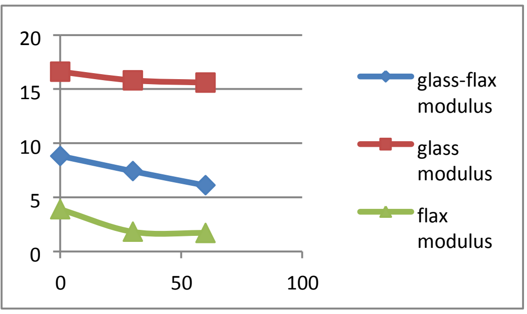
14.3. Are figures readable?: yes, this is fine

14.4. Figure 2: Indicate with arrows and descriptions what can be seen on these images. The images are not at all self-explaining.

A: As suggested, We revised figure 3 (old figure 2) and also modified the results and discussion section, accordingly.

14.5. Table 3 and 4 and 5: convert it into a point-line diagram





A: Thanks for Your suggestion. Tables 3-5 were converted into a point-line diagram.

15. Equations:

15.1. Please describe EACH formula symbol in the text (e.g. v.v. as volume void fraction)

15.2. Equation (3): Delete the % in the brackets and instead include it after the ‘100’.Then it is mathematically correct (100*%=100/100=1).

A: We checked eq.1-3 following to Your suggestion.

16. Statistics:

16.1. Are statistics well described? : it is not clear, which experiments were repeated and if they were normally distributed. Only then, you are allowed to use the standard deviation.

A: The replicas for each test was reported in “Material and methods”.

17. General remarks:

17.1. A laminate is a flat material made of two or more layers. What I understand, is, that only the Fiber/Glass material is a laminate. Each layer in this laminate is a composite then. Thus, you only have one laminate! (E.g. P10, L44: “glass laminates…” →this is not a laminate then, it is only the glass fiber composite) Please check this throughout the text. Also it is not clear to me, how you produced this laminate.

A: We have tried to make clear that glass and flax composites are also made of laminas constituted by fabric fiber and epoxy resin. In this sense, after this clarification all

batches could be identified as laminated, although some of these are made up by identical laminas. We hope that the approach, proposed in this form, is compatible with the Reviewer's requirements.

17.2. Check the use of tenses, especially in the methods section ("were exposed…had a chemical composition …. is 35°C")

A: We apologize. We revised this section. Thank you for the suggestion.

17.3. Replace "vegetable" fibers with "natural" fibers or "lignocellulosic fibers" → be consistent

A: Done

17.4. Please explain after each section, what the findings mean for the application in marine environment. Does it solve the existing problems? Avoid the usage of weak adverbs such as "good, worse, better…" State clear numbers.

A: We checked the article according to your consideration.

17.5. You are talking a lot about cracks in the material. Did you ever clearly observe cracks under the SEM? Which size do they have? Do you have images? Add them.

A: We apologize for this lack. In the revised version we modified figure 3 (old figure 2) and the related results discussion in order to better relate descriptions with SEM images.

17.6. Often you use the word "degradation". Please explain in the introduction, what exactly you intend to say with this word. There are many different meanings of the word. Sometime I have the impression, that you do not mean degradation but decrease.

A: Following Your suggestion, We revised the whole manuscript avoiding where possible "weak" terms.

17.7. Some images would be quite helpful. (see below)

A: According to your following suggestions, We added four images (related to stacking sequence, water diffusion scheme and mechanical results) in the revised version.

Special remarks:

18. **P3, L14-20:** sentence is not understandable

A: We revised this sentence as: "For the sake of comparison, also full flax and glass epoxy composites were investigated. All samples were exposed to salt-fog environmental conditions, according to ASTM B117 standard, up to 60 aging days."

19. **P4, L3-8:** This sentence sounds a little bit like you would try to put a high amount of "intelligent" words into one sentence. What do you want to say? If you turn it around, it would be clearer "Choosing suitable and effective materials in terms of performance, durability and environmental impact is challenging. A special area of interest is the identification of composite structures suitable for marine structural applications". Still it is not really clear to me, what's the important point in this sentence.

A: Done

20. P5, L34-36: Do you really have a look at the fiber stacking sequence in your manuscript? If not, there is no need to mention this. The introduction is like a mini review and sometimes repetitive.

A: We revised this part in order to avoid misunderstanding

21. **P6, L55:** you could mention, that the difference between the experimental density and the theoretical density is, that the experimental density includes the void volume fractions and should thus be lower. This increases clarity.

A: Thank you for this suggestion. It was done.

22. **P7, Table1:** what do the footnotes in the stacking sequence mean? If they are not important in the manuscript, delete them.

    A: The footnotes in Table 1 have been added only for clarity regarding the warping type of all fabrics used in sample preparation.

23. **P7, Table 1:** How did you measure the thickness?

    A: The thickness was measured by using a digital thickness gauge.

24. **P7, Table 1:** You calculated the different densities. But what is your interpretation? Did you ever use and interpret these values in the text?

    A: the difference between the experimental density and the theoretical density was used to determine the void volume fraction in the composite laminates. These considerations were added in the description of table 1.

25. **P7, L49:** "extracted" = "the separation of a substance from a matrix" → check wording

    A: We apologize, we checked this sentence.

26. **P7, L56:** Silica will not only avoid further degradation but instead remove moisture from the composite! This changes your material!!!!

    A: We avoid for the mistake. Off course we agree with you consideration. All samples were treated according to ASTM D570 standard (related to water absorption of plastics) and then stored at room temperature. We clarified this point in the experimental part.

27. **P8, L2: Why were the cleaned? This affects the water content?!**

    A: The water absorption of composites was simply measured during the salt-fog exposition by periodically removing samples from the climatic chamber, cleaning (with a dry cloth) and weighting them by using an analytical balance. No standard is available for monitoring the mass change of materials aged in salt-fog environment. An internal protocol was applied according to ASTM D570 standard related to water absorption of plastics during long term immersion tests.

28. **P8, L22:** what did you actually measure? The angle? Surface tension? Did you measure time dependent or after e.g. 3 seconds?

    A: The procedure concern at first to realize a video of 15s of the droplet after the deposition. Afterward the instrument software automatically identify the droplet shape and it determine the contact angle during time (15s). The average contact angle valued of 15s of deposition was used. This aspect was clarified on the revised version.

29. **P8, L32:** Which software did you use?

    We reported in the article that it is OneAttensio software by Biolin Scientific

30. **P8, L47:** "prismatic"? Do you mean "rectangular"? 32. **P8, L52:** "cross-head" → "cross-head speed"

    A: Done

33. **P8, L52:** why 5.12 mm/min?

    A: The speed was chosen according to ASTM D 790 where the cross-head rate was exstimated based on sample geometry.

34. **P9, L5: prismatic? Rectangular?**

    A: Following Your suggestion, "prismatic" was replaced with "rectangular"

35. **P11, L10:** what are "preferential pathways in the polymer chains"? Check Fick's and Henry's law.

    A: We modified this sentence indicating that the preferential pathways are favored by the presence of hydrophilic areas due to local unreacted resin portions.

36. **P14, Fig3:** the horizontal lines for M∞ seem to be arbitrarily chosen. Especially for Glass and Glass-Flax

    A: The horizontal lines in figure 4 (old figure 3) were calculated considering the last 4 acquired point in the water uptake curve. We agree that this option created a discrepancy mainly in glass-flax laminates. Although, it is our opinion that this difference can be considered acceptable taking into account the error bar as reported in figure 2 (old figure 1). We hope that the figure 4 in the present version could be considerate suitable by your opinion.

37. **P16, L15:** Please check a paper about hygroexpansion, where effects are extensively reviewed: "Factors affecting the hygroexpansion of paper"

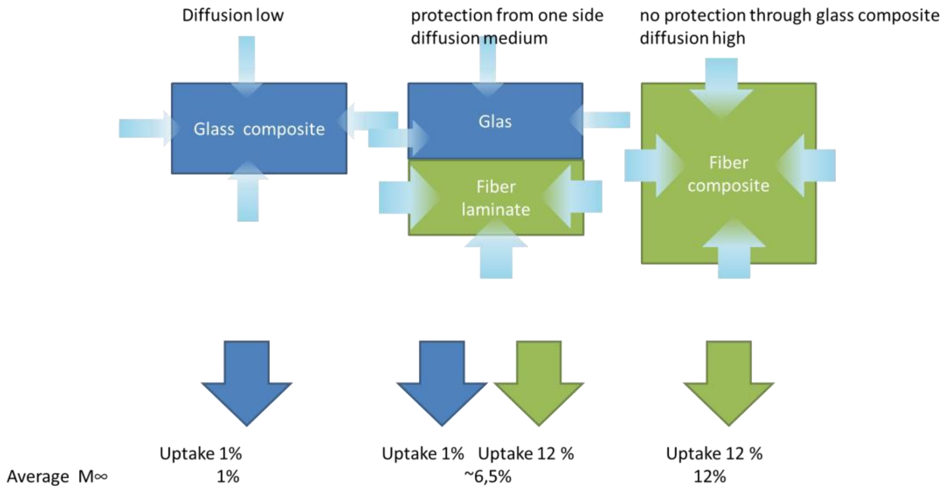
    A: Thank you very much for the information. The article is very interesting and details significantly the hygroespansion phenomena in natural fibers. Based on new knowledge, we also added a sentence and the reference to this article.

38. **P16, L17 ff**, This was already described in page 11 and also on page 17, repetitive!

    A: We apologize, according to your suggestion, We significantly reduced the emphasis of this sentence.

39. **P9, section 3.1:** As you are dealing with a laminate, there is no use of calculate a diffusion coefficient for the material. It only makes sense, to calculate a diffusion coefficient for a monolayer. Comparing the slope in figure 1, it can simply be stated, tha

    (a) glass uptakes almost no water
    (b) flax uptakes a lot more water
    (c) as one side of the flax composite is protected by the glass composite, the uptake is only half as fast
    (d) as presumably (this was not mentioned so far but should be done!) the glass composite layer and the fiber composite layer have a similar thickness, the final percentage water uptake is obviously only half for the flax-glass in comparison to the flax composite.



    By assuming such averages, you could even try to interpolate the values, which would give you an advance as you do not need to make experiments for each combination.

    A: Thank you so much for Your contribute. According to Your revision, We added a sentence in the discussion of the results clarifying this point. Based on your schemed figure, We also added figure 4.

40. **P17, L24:** first you state, that the value is intermediate, which is in accordance with the rest of your results. In the next sentence you state, that the fibers are completely embedded in the matrix. But then, there should be no difference between the three composites! Did you make SEM images from the surface? Then you could see, if the fibers are really covered by the matrix.

A: We agree that this consideration add confusion in the results discussion. We apologize for that. We removed this sentence in order to avoid misunderstanding.

41. **P17, L48:** How can you state, that the matrix is not relevant? Just leave the matrix away or change it to EVOH, then you will see, that the matrix does play a role!

    A: We apologize, in order to avoid misunderstaing in the revised version this sentence was removed.

42. **P17, Section 3.2**: You mix up wettability, contact angle and water absorption. Whereas the contact is ideally only dependent on the surface tension, water sorption is also dependent on voids, cracks, roughness etc.

    A: We had tried to introduce this discussion at the end of paragraph §3.2, but it is still unclear and not incisive. According to your suggestion, this concept has now been better explained in the article.

43. **P19, L10**. I can only identify a plateau for flax, not for the others.

    A: We completely agree with your consideration. We apologize for the mistake. We clarified that showing that this plateau is clearly evident for flax based laminates and can not be identified for full glass laminate.

44. **P19, L41:** "Although it is worth of noting that the contact angle values found for flax and glassflax batches are quite similar" → They are just as similar as glass and glass-flax

    A: We apologize for this misunderstanding. We revised this sentence as: "… the contact angle of glass-flax batch is slightly higher than flax one. Vice versa, the glass-flax …"

45. **P26:** Why is the storage modulus important in the application in marine environment?

    Storage modulus (E") integrated with the information acquired on the elastic modulus (E'), in our opinion, can provide information on the dynamic behavior of the material but also on the adhesion properties at the fiber/matrix interface (considering that tand = E "/ E '). These information are useful to better understand the durability performances of the composite laminates in severe environmental condition as in marine applications.

46. **P27, L5:** "lowering the degradation in the storage modulus" → Do you mean the "decrease" in the storage modulus? Check wording!

    A: Sorry for the misunderstanding. "degradation" was replaced with "decrease";

47. **P29, L40:** "Figure 7 it is worth nothing"???

    A: We apologize. We revised this sentence.

48. **P30, L10:** The objective "evaluation" is a weak objective. It is just like "observing". Isn't it rather the goal to understand, what's happening in order to be able to extrapolate results, to find a new material, to improve material properties….?

    A: We agree with your consideration. We modified "evaluation" with "assessment". This modification was proposed also in the tile of the paper.

49. **P30, L30:** "and modulus be + 128 %" -- > by 128%

    A:The suggested corrections were done.

50. **P31; L1:** How do you define a "good" compromise? Good is a weak word.

    A: We agree with Your consideration. We modified "a good" with "an effective and suitable".

Reviewer #2: The manuscript entitled "Experimental evaluation of the aging behavior of flax/glass hybrid composites for marine applications" focus on the aging property of the hybrid composites. Three different kinds of the composites including the flax composite laminates, the glass composites laminates and the flax/glass hybrid composites laminates were compared to show that the flax/glass hybrid composite laminates exhibited a good compromise in terms of environmental impact, mechanical properties, aging resistance and cost between flax and glass composites. Although the results are predictable and pretty straight forward, this paper still provided systematic experimental research for reader to understand the aging behavior of the flax/glass hybrid composites. Therefore, I think this paper could be accepted after minor revision.

I have some revision suggestions for the manuscript:

1. All the tables should be expressed by using the three lines table.

A: We modified them by using the three lines table format.

2. Page 7, line 52: "the cross-head" should be change as "the tension speed"

A: The sentence was corrected as suggested by the Reviewer #1.

3. For figure 2 and figure 6, the label should be listed on top left corner not on right corner, at the same time, the label should be magnified to see more clear. The clear bar should be added into the bottom right corner of SEM figure instead of only using the original bar of SEM figure.

A: Figures 2 and 6 were modified as suggested by the Reviewer. Moreover, following the suggestion of the Reviewer #4, these figures were merged (Figure 3 in the revised version)

4. Page 12, line 42: the word "respectively" should be added on the end of sentence.

A: The suggested correction was done

5. Figure 5, the label of the horizontal axis should be changed as "Time [d]. For the vertical axis, the label should be expressed using Strength Retention [%], Modulus Retention [%], corresponding 0, 20, 40, 60, 80, 100, 120, 140.

A. Thanks for your suggestion. Figure 5 was properly modified (Figure 8 in the revised version).

6. Provided the object images of flax, glass and glass-flax laminates in the manuscript.

A: We added figure 1 where three reference samples are reported.

Reviewer #3:

The authors attend for the environmental aspects of the use of natural fibers for the composites reinforcement and in the other hand still consider glass fiber in the composition of the developed material.

That will also apply for the same environmental problems, because the new developed material as proposed contains non degradable fibers as well. The only truely authentic improvement would be in the case of total ellimination of glass fibers in the composition. Please explain in the environmental aspects the advantages of developing such natural fiber/ glass fiber composite.

The work is interesting and relevant for the developing of alternative materials for the use in the marine industry, specially in the economical aspects.

A: Thanks for the compliments. Furthermore, according to your suggestions, the introduction was revised in order to better clarify the relevance of improved knowledge on durability of hybrid flax/glass composite laminates.

However, it is quite not current. The flax fibers (or any other lignocellulosic fiber) should have been replaced by cellulose nanofibers. Thus it is known that composites having cellulose nanofibers present superior performance in all aspects evaluated in this article

A: Thank you for the reviewing comments and appreciate evaluation of the article. We agree with your consideration that a possible development is to investigate the performances of cellulose nanofibers based hybrid composites. Their use is potentially effective and suitable to improve performance stability. It could be a possible research activity to develop in future steps.

Reviewer #4: Authors performed systematic experiments on a research topic of interest. In spite of that the authors have published some similar works recently, they were trying to draw a border to guaranty the novelty of their results. The paper is well organized and after its recent modification it is ready to publish.

A: Thanks for the compliments

However, before publishing the authors need to use a high-quality figures (increase the quality of Fig.1, Fig.3, Fig.4 and Fig 8).

A: Following the suggestion of the Reviewer, the resolution of the figures was improved.

Put the SEM images of aged and unaged samples next to each other (Fig.2 and Fig.6 should be shown in a figure).

A: Figures 2 and 6 were merged as per suggestion of the Reviewer (Figure 3 in the revised version).

Also, the authors should insert the error bar for each graph in Fig.3.

A: We apologize but the purpose of figure 3 (after the revision figure 4) is to highlight the diffusion parameters for each composite laminate batch. We had evaluated, during the first submission, the possibility to add the error bar in the markers, as in figure 2. However, in order to increase the figure readability, it was decided to not show it in this figure.