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Characterization of Bio-Epoxy Composites with Mussel Shell Powder and *Posidonia* Fibers

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Abstract

Bio-epoxy composites were fabricated by casting a resin–hardener–filler mixture into 3D-printed molds, using different sea-originated secondary raw materials: mussel shell powder (MSP) (63–83 μm) and *Posidonia oceanica* short fibers (POF) (1–2 mm). Monofiller composites were prepared with 5 or 10 wt.% MSP, or 5 or 10 wt.% POF. Hybrid formulations were also produced, containing both MSP and POF in two combinations, where the total amount of filler again summed up at 10 wt.%. A subset of the samples was conditioned by immersion in a 35 ‰ NaCl solution reproducing seawater composition until saturation was reached. Characterization was carried out on unconditioned and conditioned samples by Shore D hardness and Charpy impact tests while performing three-point flexural loading only on unconditioned ones. Fracture morphology was also investigated. Adding MSP slightly enhanced resin hardness, whereas impact absorption exhibited, to a variable extent, a two-phase behavior, reproducing crack initiation and propagation. The MSP6-POF4 hybrid configuration provided the greatest improvement in absorbed energy (25–30% higher), which was retained after conditioning. The introduction of fillers, first separately, then in combination, resulted in a reduction in flexural strength to a similar extent for all unconditioned configurations. Finally, composite panels containing 10 wt.% MSP, 10 wt.% POF, and a 6MSP–4POF hybrid formulation, intended for prospective boat deck applications, were fabricated and compared with neat bio-epoxy, showing satisfactory consolidation. Density and post-molding dimensional shrinkage were measured on the panels.

Keywords: mussel shell powder; *Posidonia* fibers; impact characterization; hardness measurement; seawater conditioning

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1. Introduction

The idea of introducing biological marine waste generated by anthropogenic activities (such as seafood consumption [1], beach nourishment [2], or seaweed removal [3]) into composites has been proposed as a way to ensure their safe disposal, without degrading the materials' properties too much. This approach would add value and potentially enhance

material sustainability, provided that the obtained materials exhibit properties suitable for practical applications. A large number of studies do already exist, which have been mainly developed in recent years, reflecting the growing interest in sustainable materials and circular economy-driven solutions [4]. In this context, attention to the bare reuse of marine waste as filler or reinforcement, as well as considering their combination with environmentally friendly polymer matrices, has progressively increased. Therefore, the use of bio-based resins is increasingly preferred for composite fabrication [5].

Biological marine waste can generally be classified into two main categories: polysaccharides, which are typically characterized by a high cellulose content [6], and ceramics, which are most commonly based on calcium carbonate [7]. When dealing with marine waste, a proactive approach is to develop applications in the very environment in which they have been generated. It is worth noting that in the boat fabrication sector, thermosetting matrices, such as unsaturated polyester, vinylester, and epoxy are normally used, the latter of which has been often linked to recent attempts to propose natural fiber composites in the marine environment [8]. A large market is emerging for bio-epoxies, where bisphenol substitutes for the synthesis of the epoxide ring are extracted from vegetable oils, though it is fair to say that in a considerable number of these, the bio-based content is still limited [9].

Several studies have proposed the use of different kinds of sea and fishery sector waste, namely, stranded Posidonia [10,11] and mollusk shell powder [12,13], a notable source of biogenic calcium carbonate [14] which shows significant performance in composites, yielding, in particular, a higher hardness and wear and abrasion tolerance [15,16]. This is linked to the inherent characteristics of the calcareous exoskeleton of mollusks, which also provide significant crushing strength and toughness, such that their powder provides an ideal filler that is adaptable to both cement and polymer matrices without much difficulty [17]. A study proposed the introduction of up to 25% of mussel shells as aggregates, classifying them as limestone gravel (4–20 mm) and sand (0–4 mm) [18].

Previous research within the same project also confirmed that conditioning by immersion in 'simulated' seawater [19] and long-term exposure on the pier to account for biofouling produced limited degradation of material integrity and performance [20]. Among the three species of mollusks under consideration, the properties offered by mussel-derived calcium carbonate were proven to be slightly higher than those of other species [21], an effect likely attributable to the more effective combination of calcite and aragonite crystals within the shell structure [22]. On the other hand, the introduction of Posidonia in the form of short fibers in a partially bio-based matrix has already been proposed. This occurred, for example, in poly(butylsuccinate) (PBS), which proved particularly suitable for fibers with a significant amount of holocellulose, which was measured to be in the region of 60% in *Posidonia oceanica* [23]. However, inserting PO fibers into a polymer matrix has not always proved straightforward due to its tendency to agglomerate, which indicates potential, e.g., in acoustic panels application [24]. This limitation can be mitigated, while avoiding chemical treatments, by carefully controlling fiber length down to a few millimeters [25]. A systematic comparison between monofiller and hybrid MSP–POF/bio-epoxy systems, including post-conditioning impact response and demonstrator-scale panels, however, is still missing.

In the present work, bio-epoxy composites filled with mussel shell powder, *Posidonia oceanica* short fibers, or a mixture of the two, were fabricated. These were characterized in terms of Shore D hardness and Charpy impact properties, both in the as-received and after immersion to saturation in a 35 ‰ saltwater solution, after which the flexural strength on the unconditioned samples was also measured. Following this, panels with different configurations were fabricated and compared to analyze their functional response. The purpose of this work, introduced in a field of growing interest, is particularly to explore the

combination of the two calcareous and polysaccharide-based fillers, respectively, in a bio-based matrix to complement previous studies. The expected advances of this study involves the blended application of the two different fillers, which requires various degrees of contact with the matrix; in the case of Posidonia, to avoid the phenomenon of agglomeration that would impede creating the composite by excessive void content [26].

For the two fillers, different criteria were followed, in the sense that for the ceramic, the smallest possible fraction was used, whilst for *Posidonia oceanica* fibers, attention was drawn to the potential to obtain lengths that were sufficient to provide some reinforcement effect, avoiding the aforementioned agglomeration risk as much as possible.

2. Materials and Methods

2.1. Raw Materials

The calcareous exoskeletons of *Mytilus galloprovincialis* (Lamarck, 1819), native to the Adriatic Sea, were collected, thoroughly washed, and freed of protein residues, then ground with a jaw mill and sieved (Figure 1A). The very low level of protein contamination was measured in a semi-quantitative way in data collected by Raman spectroscopy, as in Latini et al., 2025 [27], through the respective height of phenylalanine amino acid vs. calcium carbonate signal, leading to a contaminant content of $0.45 \pm 0.07\%$.

Figure 1. Raw materials used in the composite manufacturing: (**A**) mussel shell powder (*Mytilus galloprovincialis*); (**B**) *Posidonia oceanica* short fibers obtained from egagropili; (**C**) bio-epoxy resin system (Entropy Super Sap CCR/CCF).

Posidonia oceanica fibers were obtained from egagropili, collected in Bay of Kotor (Montenegro), and washed to remove as much silica and salt as possible (Figure 1B). Subsequently, fairly aligned ribbon-like fiber filaments were obtained, which were then cut. A commercially available bio-epoxy system (Super Sap CCR Clear Casting Resin with CCF Clear Casting Fast Hardener by Entropy Resins, Genova, Italy) was used. The resin, containing 29% bio-based carbon, was thoroughly mixed with the fillers and processed using a vacuum molding technique (Figure 1C).

Table 1 identifies the essential properties of the epoxy casting resin system used in composite manufacturing.

Table 1. Main physical and processing properties of the epoxy casting resin (CLR, slow hardener).

Property	Value	Notes
Resin type	Epoxy casting resin	Transparent system for thick castings
Hardener	Slow-curing amine-based hardener	Extended pot life

Table 1. *Cont.*

Property	Value	Notes
Mixing ratio (by weight)	100:60	Resin:hardener
Viscosity (mixed system, 25 °C)	~600–800 mPa·s	Suitable for filler impregnation
Pot life (25 °C, 100 g)	~40–50 min	Enables controlled mixing and degassing
Curing temperature	Room temperature	No post-curing required
Full curing time	~24 h	At 20–25 °C
Glass transition temperature, Tg	~55–60 °C	Typical for casting epoxies
Flexural Strength	~93.1–100 MPa	Cured resin
Flexural Modulus	~2.9–3.0 GPa	Cured resin
Density	~0.98–1.14 g/cm^3	Hardener and resin densities respectively

2.2. Composite Manufacturing

The composite preparation method followed the procedure reported in Fragassa et al. [19]. A hand casting procedure was used, slowly mixing the fillers to prevent the formation of agglomerates, followed by a curing phase at 25 ± 2 °C with continuous control of the process conditions. Untreated *Posidonia oceanica* (PO) fibers were extracted from egagropili and reduced in length (<2 mm) using a chopping mill type Retsch SM100, Haan, Germany. Mussel shell powder was ground using a jaw mill and sieved between 2 mm and 63 µm. Larger particles were used to fabricate geopolymers, as reported in Latini et al. [27]. In contrast, for the fabrication of composites in this work, only a small fraction between 63 and 83 µm was employed; this is indicated in Figure 2.

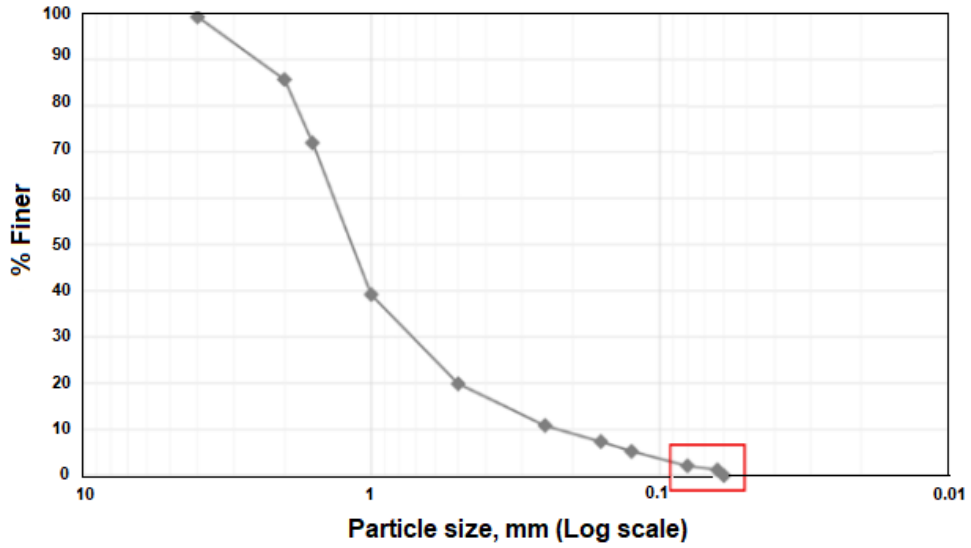

Figure 2. Mussel seashell granulometric curve. The red square indicates the granulometry used in the present work.

POF images were acquired with a *sCMEX* camera by *Euromex* (Arnheim, the Netherlands) using *ImageFocusAlpha* software (Version 1.3.7.29179) and later analyzed using *ImageJ* software (Version 1.54) with a pixel-to-micron ratio equal to 2. Blurry, superposed and/or irregular fibers were not taken into account for the calculation to reduce measurement errors. These images have been employed to evaluate PO fiber properties; for example, maximum (max) ribbon width and minimum (min) aspect ratio (length over diameter)

were calculated. Collected data were statistically treated using PyCharm software (Version 2025 1.3.1).

The samples were analyzed before and after conditioning in a laboratory-prepared saline solution used to simulate marine conditions (35 g/L NaCl solution, at room temperature, until saturation was reached) [19]. For this purpose, two groups were considered: for each of the compositions, as detailed below in Table 2, 10 samples were analyzed in the as-received condition and 10 samples were analyzed after conditioning; these are hereinafter referred to as 'unconditioned' and 'conditioned' samples, respectively.

Table 2. Series of samples with relative compositional percentages for Shore D hardness and Charpy impact tests.

Series	Bio-Epoxy Resin (wt.%)	MS Powder (wt.%)	PO Fibers (wt.%)	Bio-Based Content (wt.%)
NE	100	0	0	29
MSP5	95	5	0	33
MSP10	90	10	0	36
POF5	95	0	5	33
POF10	95	0	10	38
MSP8-POF2	90	8	2	36
MSP6-POF4	90	6	4	36

Specifically, the composite samples were fabricated by pouring the mixture into 3D-printed molds with dimensions of 80 × 15 × 15 mm (18 cm^3), in accordance with the ISO 179 standard [28]. As shown in Table 2, the investigated configurations included neat bio-epoxy (NE), composites filled with 5 or 10 wt.% of mussel shell powder (MSP5, MSP10) or *Posidonia oceanica* fibers (POF5, POF10), and two hybrid formulations combining both fillers (MSP8–POF2 and MSP6–POF4). The natural filler content in the last column adds up the bio-content of the resin to the percentage of biogenic fillers. Polymer bars for three-point flexural testing were also produced, again in a total of 10 per configuration, using various amounts of filler, namely, MSP6, POF4, and a combination of the above, again obtaining the MSP6-POF4 hybrid. Samples had an average size of 150 × 13 × 3 mm, which was suitable for the evaluation of the flexural resistance (ASTM D790) [29].

Demonstration panels, specifically designed (i.e., thickness and overall dimensions) for the production of boat seats, were developed using a silicone rectangular mold (Figure 3) with the dimensions 300 × 200 × 4.5 mm. The curing process leading to the full resin crystallization was carried out at room temperature (18–22 °C) for 20–22 h. To prevent air ingress and bubble formation, the mixture was homogenized by scraping all the surfaces of the container in which they are placed to avoid air incorporation. In this case, the following compositions were preferred: NE, MSP10, POF10 and MSP6-POF4.

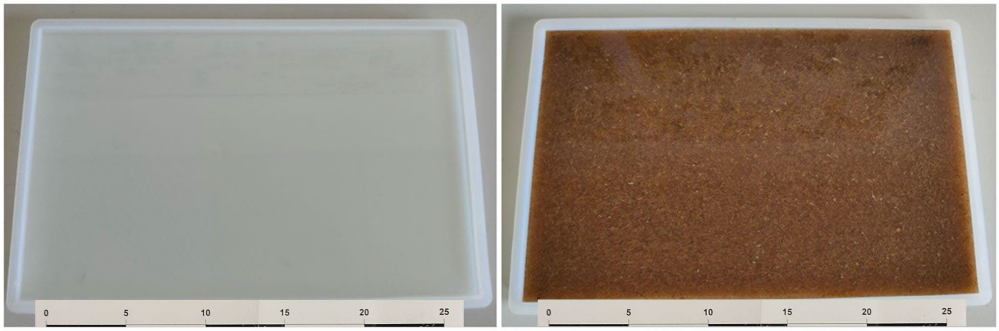

Figure 3. Silicone mold used in the production of panels and curing panels. The scale bar is in the range of centimeters.

2.3. Material Characterization

The fabricated composites were characterized to evaluate their morphological features and mechanical performance, both before and after conditioning.

Optical microscopy observations were performed using an Iscope Euromex system with a maximum 50× magnification in transmitted light on PO fibers.

Scanning Electron Microscopy (SEM) observations were performed using Field Emission Scanning Electron Microscopy (FE-SEM) equipped with a backscattered detector (BSD) (Sigma Family, Zeiss, Jena, Germany) to obtain high-quality microphotographs of PO fibers.

Regarding the breaking surface of the composites, macro-photographic observations were carried out with the acquisition of high-resolution images with an EduBlue Stereo Microscope (Euromex, Arnhem, The Netherlands) with 5× or 10× magnification.

Charpy impact tests were carried out by using an instrumented pendulum with an accuracy of 0.01 Joules according to the ISO179 standard [28]. Shore D hardness was measured on the impacted half-specimens, according to the ASTM D2240 standard [30]; considering that the sample thickness was higher than 6.4 mm, as prescribed by the standard: thence, 20 measurements per category were obtained. Flexural testing was performed using a Zwick–Roell Z050 electro-mechanical machine using a 5 kN load cell at a crosshead speed of 3.67 mm/min.

On the demonstrator panels, post-curing volume shrinkage (%), density (g/cm^3), and thickness (mm) were measured. For volume shrinkage, the following equation was used:

$$\Delta V = \left(\frac{V_f - V_i}{V_i} \right) \times 100$$

where V_i indicates the initial volume and V_f the final one. Initial and final volume, as well as thickness variability measured at the panel edges, was obtained by using a millimeter caliber. The average thickness was calculated by taking a minimum number of ten measurements over the surfaces of each panel.

3. Results and Discussion

The potential for the introduction of *Posidonia* fibers into the reinforcement of composites mainly depends on the achievable aspect ratio and its ability to provide sufficient adhesion with the resin. The set of fibers extracted from PO leaves were observed by SEM to analyze the surface morphology, showing epidermal cells with elongated and thread-like shapes arranged in parallel, in which the typical ribbon-like geometry (flattened section) is highlighted, as was also recognized in [31] (Figure 4).

The difficulty in performing measurements of the PO fibers' geometry arises from their high heterogeneity. Observable materials include almost intact fibers and elementary fibrils [32] (Figure 5A,B). The fibers also appear heavily damaged after the mechanical reduction. The typologies of damage observed included ubiquitous fiber splitting, normally defined as fibrillation (Figure 5C); bifurcations and irregular borders; and dispersed sheet-like (Figure 5D) materials and filaments derived from the reworking of the fibers. On the one hand, to avoid agglomeration, the dimensions of the fibers need to be reduced, yet, due to purposely avoiding chemical treatment at this stage, it is likely that their mechanical performance would be affected.

Results for the calculation of PO short fibers properties, including average length, maximum ribbon width and minimum aspect ratio, are shown in Table 3. The analysis was conducted over 64 fibers after the removal of evident outliers. The overall variability of ribbon width in fibers is ±8.54 µm and relative range of variability is 1.3–27.9 µm. The calculated minimum aspect ratio (Figure 6) is in the range of 3.0–28.6, with a mean value of 13.6 ± 5.7. The main limitation of the measured values is the difficulty in measuring

the fiber diameter using a two-dimensional image. Reported values only account for a preliminary investigation of PO short fibers' properties after mechanical reduction. Further studies will aim to obtain three-dimensional images for PO fibers in order to accurately calculate fiber diameter, thus obtaining a higher accuracy in the measurement of the aspect ratio. The measurements indicated values lower than what can be achieved by extracting nanocellulose from POF, as carried out in [33], where at the expense of a considerably less sustainable chemical process (use of 6.5 mol L^{-1} sulfuric acid), an average aspect ratio of 35 was obtained. It may be nonetheless suggested that in most cases, the aspect ratio of the fibers is able to offer some reinforcement and not just a filling effect to the epoxy matrix. However, in a more general sense, a lower aspect ratio, such as that measured in [34] with tiger grass, barely changes the fiber–matrix interaction; therefore, its suitability is dependent on the application envisaged.

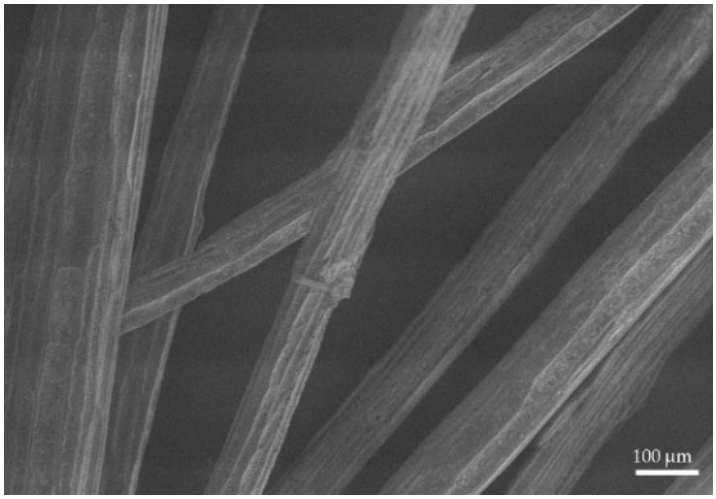

Figure 4. Surface morphology of *Posidonia oceanica* fibers by Scanning Electron Microscopy (SEM).

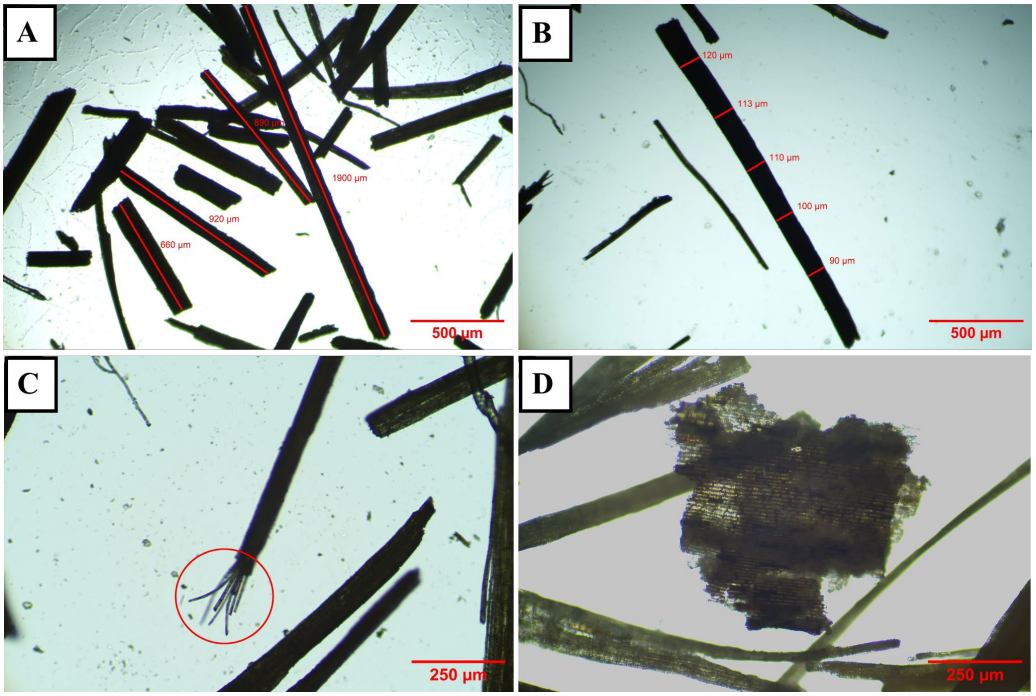

Figure 5. Optical observation of PO fibers and acquisition of fiber diameter. (**A**) Posidonia fibers of different length (lengths barred in red); (**B**) Example of diameter measurement along the fibers; (**C**) Fiber splitting (split area in the red circle); (**D**) Group of agglomerated fibers.

Table 3. Posidonia short fibers dimensional properties measured using *ImageJ software*.

Physical Property	Median	Mean
Length (µm)	1182.1 ± 380.5	1270.6 ± 474
Max. ribbon width (µm)	94.9 ± 16.9	99.0 ± 27.6
Min. aspect ratio	12.8 ± 3.3	13.6 ± 5.7

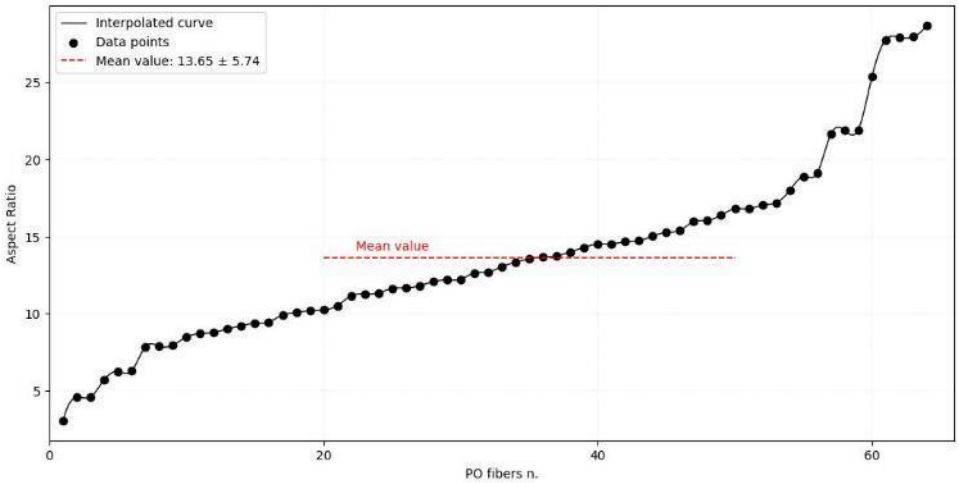

Figure 6. Distribution curve of the calculated aspect ratio for single PO fibers. On the *x*-axis, the number of fibers is indicated, while on the *y*-axis, the aspect ratio (length/diameter) is reported.

In Charpy impact testing, the pendulum, following a circular trajectory, impacts the specimens orthogonally, transferring kinetic energy and causing an initial elastic deformation until the material loses its rigidity, thus leading to fracture [35] (Figure 6). It is important to highlight that this technique only allows a qualitative assessment of fragility [36]. In our case, brittle failures were observed on all specimens at the macroscopic level, while due to the geometry of the composite, the different microscopic failure modes can be observed through nonlinear stress–strain behavior.

The Charpy impact energy of the various series of unconditioned samples remains almost constant, with values consistently ranging between 2 and 3 kJ/m^2 (Figure 7), though with a significant scattering of data. The typical aspect of the curves involves a load drop after the initial loading, which can be suggested to represent the cracking phenomenon of the sample, after which damage develops through the sample (Figure 8). This relatively stable trend indicates a uniform mechanical response of the material in its original condition, tentatively indicating that the microstructure and internal cohesion are not significantly affected by defects or pre-existing damage. However, the hybrid MSP6-POF4 shows a more complex damage absorption mode, with a higher number of peaks during impact progression (Figure 8M,N).

In contrast, the specimens subjected to saltwater conditioning exhibit a noticeably even greater variability in the measured impact energy values, yet, in some cases, there was also a considerable increase in the absorbed energy; in general terms, it is not possible to say that water absorption would affect performance at this stage. However, the increased scatter in the results is likely associated with the absorption of moisture and the penetration of saline solution into the material, which can promote internal degradation mechanisms such as microcracking, swelling, or localized weakening of the matrix [37,38]. The presence of internal humidity may therefore interfere with the energy absorption capability during impact, resulting in less predictable and reliable mechanical behavior [39]. On the other hand, it can be suggested that the limited amount of filler introduced, namely, as far as PO

fibers are regarded, might be even beneficial for the impact performance of the samples, possibly in that it allows water to travel through the material; this is also reproduced in the MSP6-POF4 hybrid samples, which was therefore selected against MSP8-POF2.

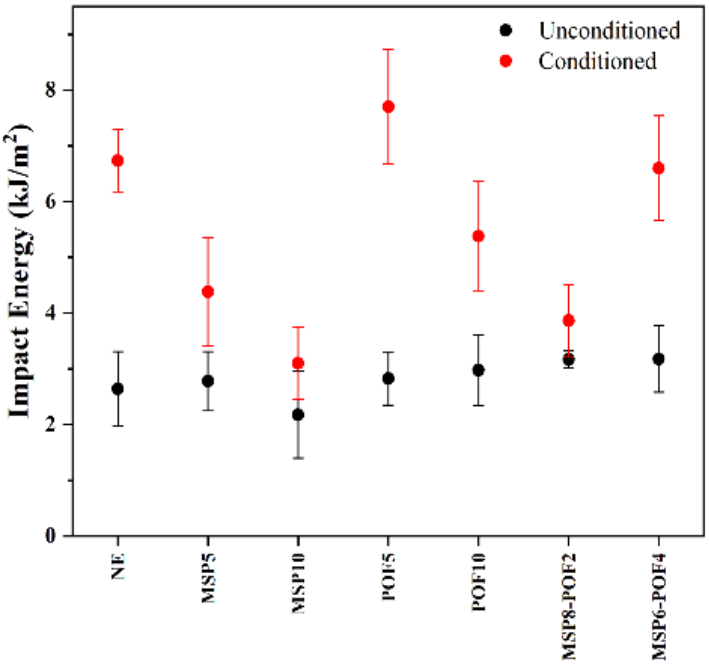

Figure 7. Charpy impact energy of unconditioned and conditioned samples.

Shore D hardness results showed no significant difference between the conditioned and unconditioned samples (Figure 9), which is promising, as it might suggest reducing the moisture effect, as already investigated in [40]. In addition, the samples containing *Posidonia*- and mussel-derived fillers did not exhibit any measurable reduction in hardness, confirming the stability of their mechanical properties even after prolonged exposure to saline conditions.

Optical microscopy observations of the fracture surfaces after the Charpy impact tests revealed no evidence of powder dispersion, basically confirming the results indicated in [41], or fiber pull-out, which was, in contrast, observed in [42], due to the much higher amount of reinforcement added, namely, 30 wt.%, which required a compatibilizer to ensure processability (Figures 10 and 11). The fillers appeared to be firmly embedded in the matrix, indicating good interfacial adhesion. In addition, a uniform distribution of both powders and fibers throughout the matrix was observed, with no detectable agglomerations or voids. This effect was particularly pronounced in the MSP6–POF4 samples, which exhibited a high degree of homogeneity in the dispersion of particles and fibers. Such an apparently homogeneous dispersion suggests quite efficient mixing and processing conditions, which might contribute to a more consistent mechanical response of the material under impact loading, despite the limited amount of filler introduced.

The flexural properties of the polymer bars with variable amounts of filler are reported in Figure 12. Generally, the introduction of fillers tends to decrease the overall strength of the samples, as depicted by the higher flexural resistance of the NE control sample with respect to filled polymers, with less evidence for those containing PO fibers. This may suggest that the variable geometry of fillers might allow them to act as defects under flexural loading [43], which suggests cautiousness in a possible future introduction of larger amounts of this marine refuse. On the other hand, an appreciable consistency of results among different specimens of a series is observed. In particular, for the hybrid series

MSP6-POF4, it can be seen that variability in the resulting resistance is low, thus indicating that the composite is quite homogeneous in terms of filler distribution in the epoxy matrix.

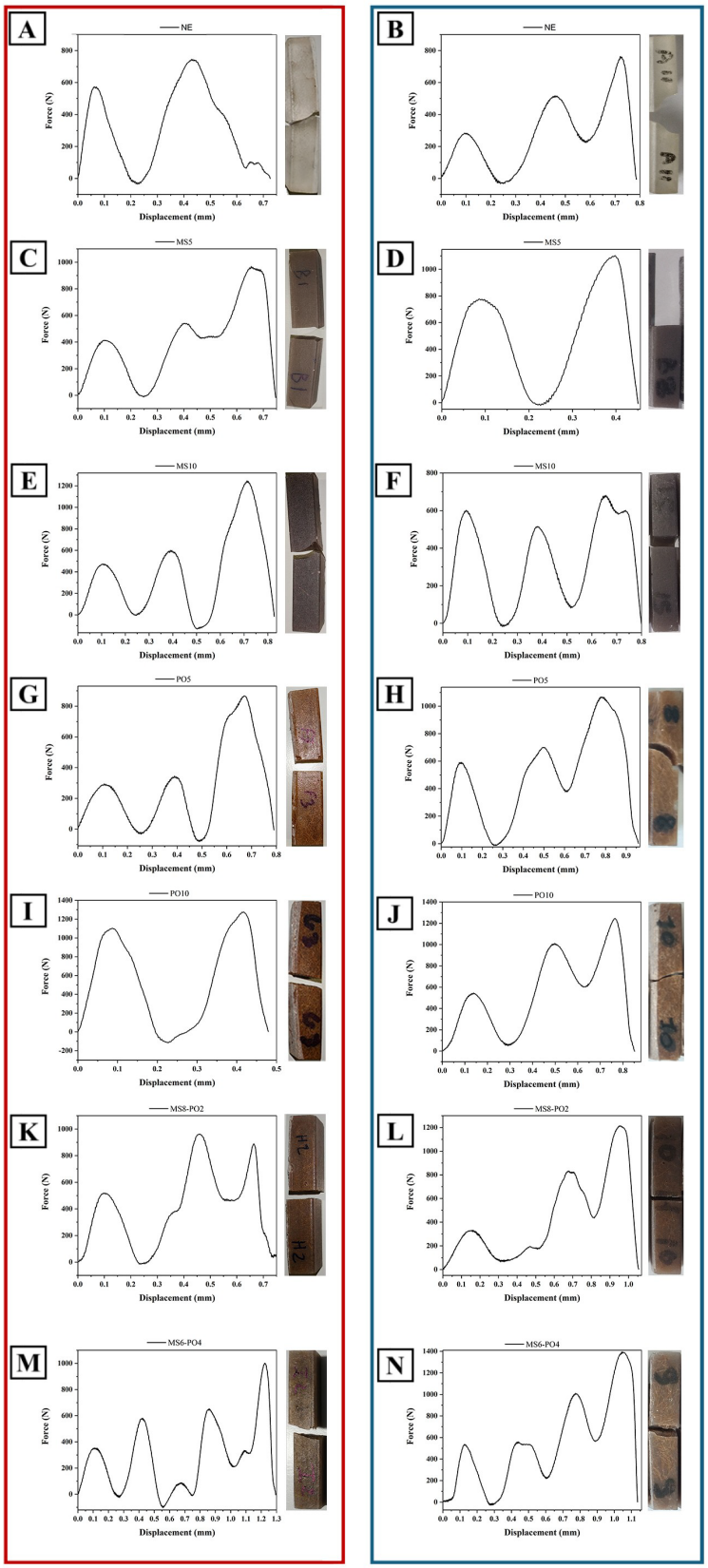

Figure 8. Charpy impact curves: red boxes indicate unconditioned samples and blue boxes indicating conditioned samples. (**A**,**B**) NE; (**C**,**D**) MSP5; (**E**,**F**) MSP10; (**G**,**H**) POF5; (**I**,**J**) POF10; (**K**,**L**) MSP8-POF2; (**M**,**N**) MSP6-POF4. Handwriting refers to the samples' codes.

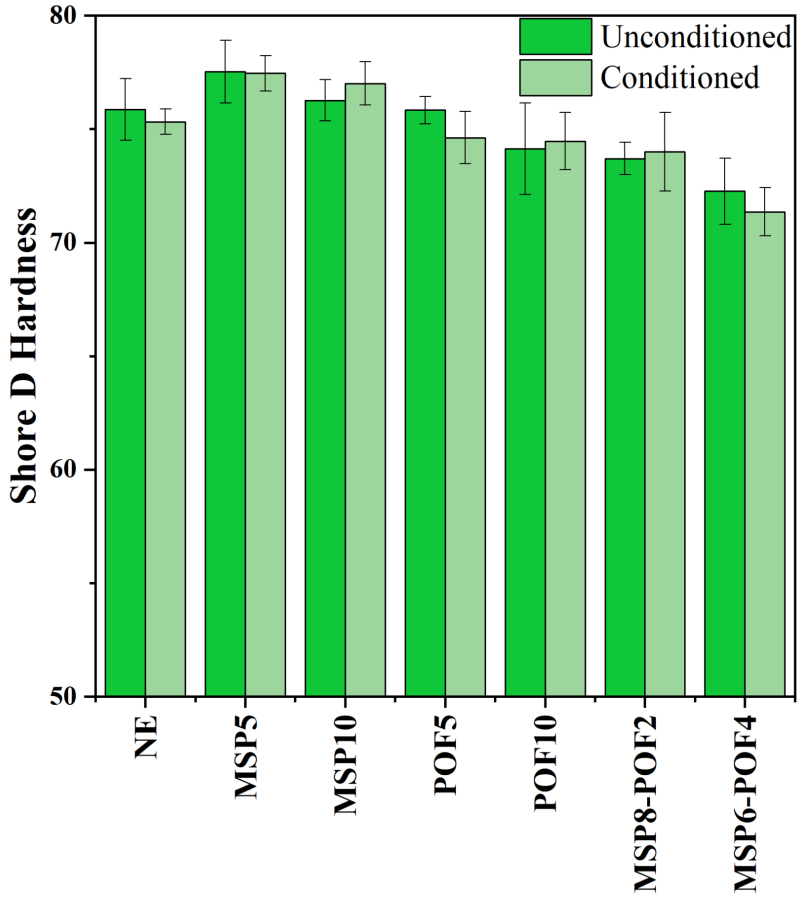

Figure 9. Shore D hardness of unconditioned and conditioned samples.

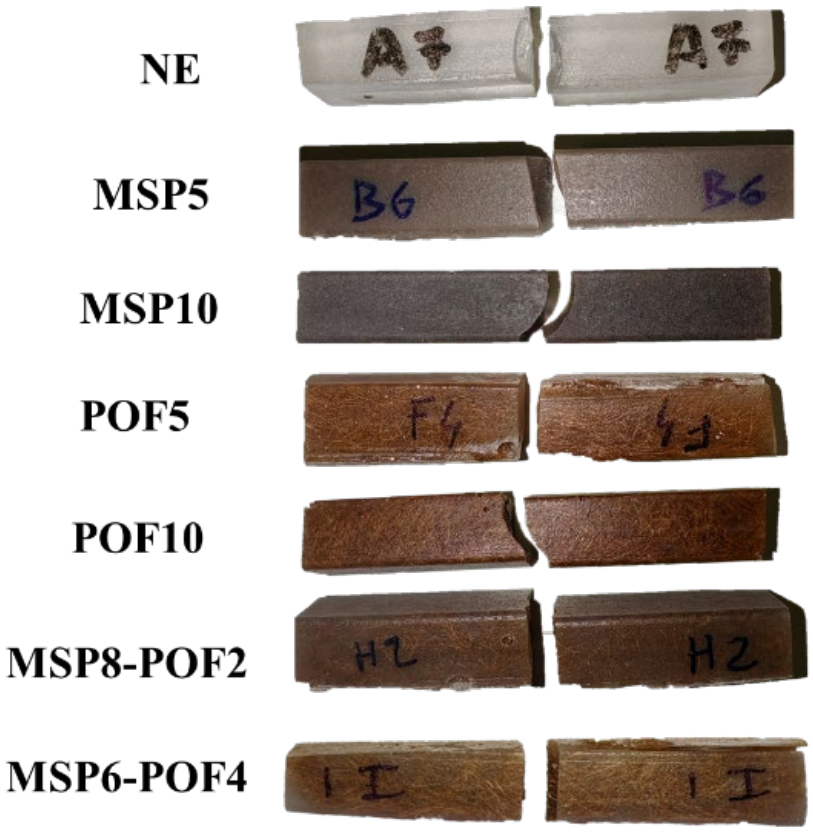

Figure 10. Typical Charpy impact specimens of the investigated composite configurations after testing.

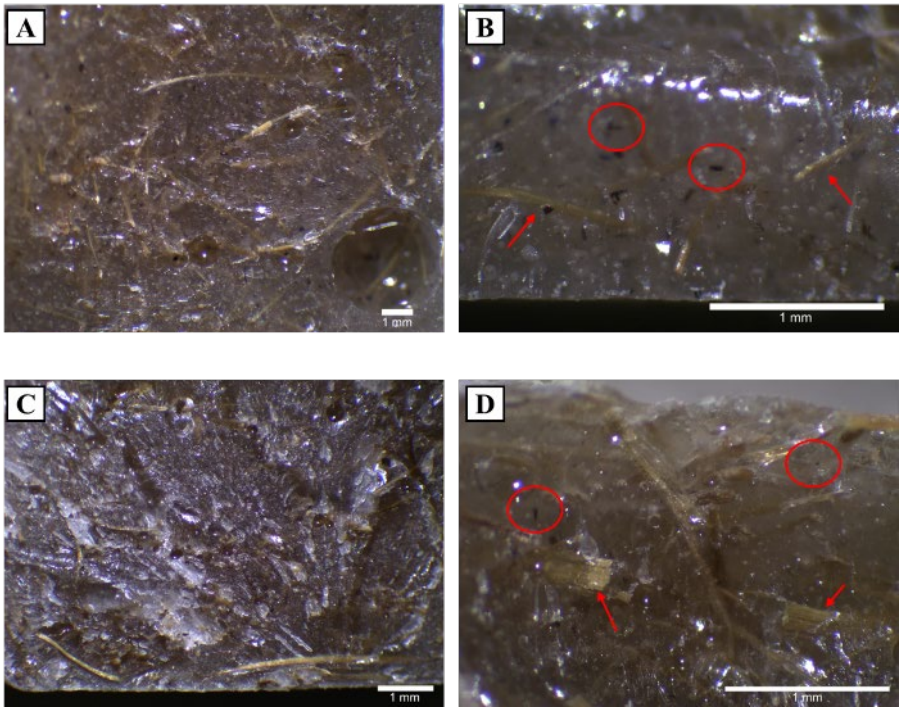

Figure 11. Optical microscopy details of the fracture surfaces after Charpy impact testing at different magnitudes in the cases of hybrid composites: (**A**,**B**) MSP8-POF2, (**C**,**D**) MSP6-POF4. The arrows indicate the presence of PO fibers, while the circles indicate mussel powder particles.

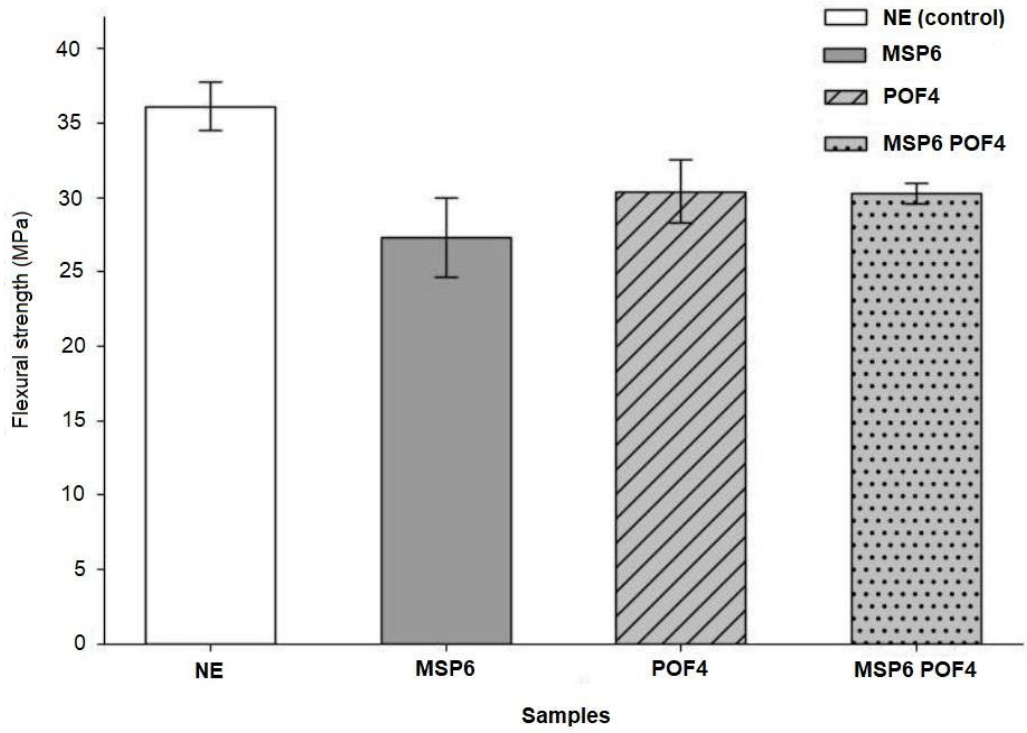

Figure 12. Flexural strength of composite samples.

Fractured surfaces microscopies of typical samples fractured by flexural loading for each category are reported in Figure 13. The unfilled epoxy sample NE (Figure 13A) displays an inherently brittle fracture surface with multiple ridges and troughs [44]. In the case of the MSP6 sample (Figure 13B), brittle behavior is still visible as well as for the other samples (POF4, MSP6-POF4) (Figure 13C and 13D, respectively), and grains of filler can be seen in the transparent matrix. These grains occupy specific areas on the sample surface,

and rather than being dispersed, these appear to be concentrated in the bottom part of the sample, possibly indicating some sedimentation phenomena, which might become of concern, in the case that a larger amount of filler is added. Bubbles and minor defects are visible on the fracture surfaces. In turn, the MSP6-POF4 hybrid laminates with both MSP and POF shows a better distribution of the seashell grain, dispersed along the sample together with the short *Posidonia* fibers.

Regarding the demonstrator panels depicted in Figure 14, their volumetric reduction values are reported in Table 4, together with their density and thickness, which were obtained by weighing the panels and measuring the final volume after extraction from the mold. The NE sample shows the highest volumetric reduction after extraction, possibly due to the reaction occurring in the matrix; a similar behavior is observed for the POF4 sample, which also exhibits slightly higher volumetric reduction compared to the formulations filled only with MSP. The latter display higher density values, which are attributable to the presence of calcium carbonate from mussel shells as filler material. In the case of the neat epoxy (NE) sample, volumetric reduction can be ascribed to the crosslinking reaction occurring between resin and hardener [45], which also contributes to the volumetric reduction observed in the filled systems. The thickness variability of the panels, reported in millimeters, indicates that panel edges tend to be slightly thinner than the central region by approximately 0.2–0.4 mm, an effect associated with resin volumetric reduction during curing, an issue only partially addressed by the introduction of fillers.

Table 4. Panels' volumetric reduction, density and thickness.

Samples	Volume Reduction (%)	Thickness (mm)	Density (g/cm^3)
NE	3.4 ± 0.6	3.7 ± 0.4	1.7 ± 0.2
MSP8	2.6 ± 0.4	4.0 ± 0.3	1.9 ± 0.1
POF4	3.3 ± 0.1	4.0 ± 0.4	1.8 ± 0.1
MSP8-POF4	2.8 ± 0.2	3.9 ± 0.3	1.9 ± 0.1

To summarize the results of this investigation, which intentionally introduced a limited amount of sea-derived filler in a bio-epoxy resin, to limit the matrix degradation, several limitations can be identified. One of these might concern the insufficient aspect ratio of *Posidonia* fibers, which may not produce an effective reinforcement effect, an issue that is widely investigated in lignocellulosic fiber composites [46]. However, the application envisaged in the marine field does not contemplate the possible use of thermoplastic matrices, which proved to be very promising in combination with PO fibers in an amount of 10 wt.%, namely, by the use of polylactic acid (PLA) [47]. In contrast, the present study did not provide particular evidence of any reduction in the brittleness of epoxy resin.

However, the production of a hybrid composite with two fillers of different origin, mussel shell powder and *Posidonia oceanica* fibers, which are ceramic and lignocellulosic, respectively, showed, if not a clear positive synergy, as in [48], at least some promise for the combination of effects, which can be improved with a more accurate dimensional control of the system. The demonstration panels produced also provide some more evidence of the possible introduction of these materials in the marine context with effective processability, through a waste valorization process from a circular economy perspective, though some aspects would then need to be addressed, such as the biofouling effect [49].

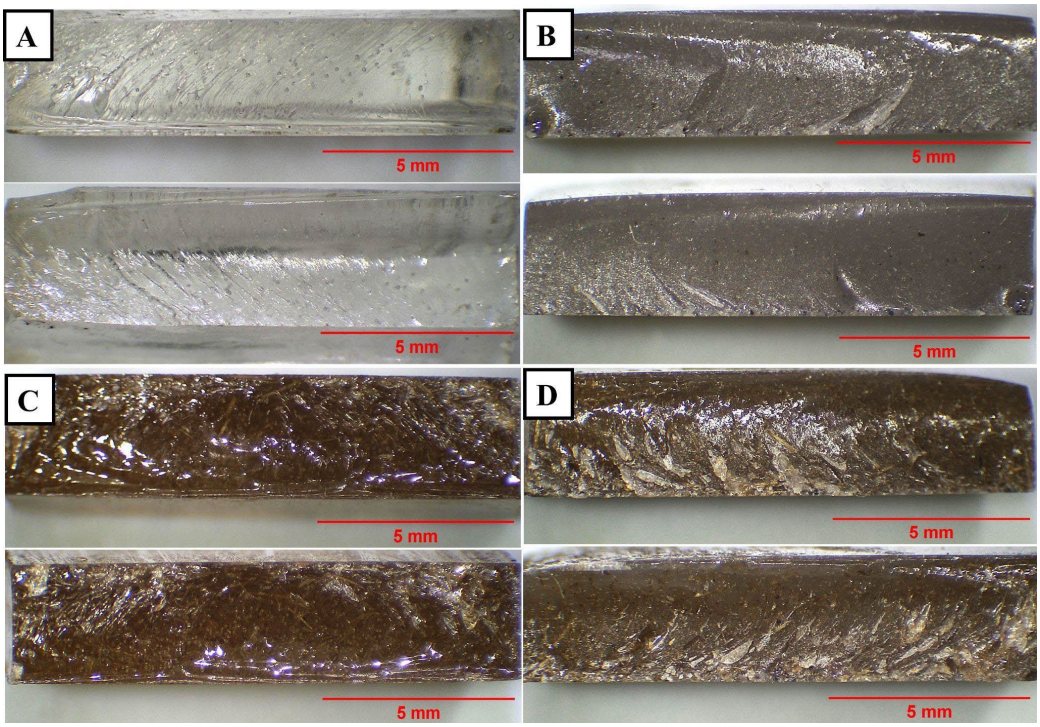

Figure 13. Optical microscope fractographs of samples tested under flexural loading: (**A**) NE; (**B**) MSP6; (**C**) POF4 and (**D**) MSP6-POF4.

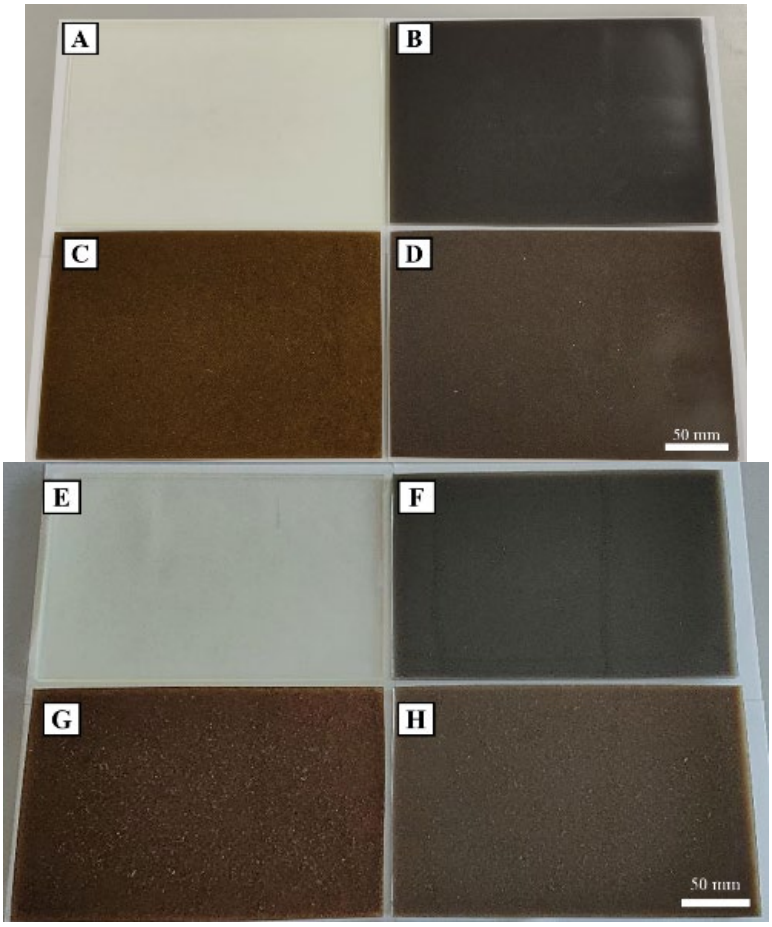

Figure 14. Front and rear surface of panels: (**A**,**E**) NE; (**B**,**F**) MSP8; (**C**,**G**) POF4; (**D**,**H**) MSP8-POF4.

4. Conclusions

In this study, bio-epoxy matrix composites containing mussel shell powder (MSP) and short *Posidonia oceanica* fibers (POF) were developed and characterized and used both individually and in a hybrid configuration with a maximum global amount of filler of 10 wt.%. Mechanical analyses showed that the addition of mussel powder resulted in a slight increase in material hardness (from 75 to 77 Shore D hardness units for 5 wt.% MSP), a result consistent with the morphological observations of the fracture surfaces. Charpy impact tests showed a two-phase behavior, wich was related to the crack initiation and propagation mechanisms, with an overall stable response in the unconditioned samples, as shown by the values obtained. Among the different formulations, the MSP6–POF4 hybrid configuration provided the greatest increase in absorbed energy, maintaining this advantage even after conditioning in saline solution, in the latter case passing from 3.1 kJ/m^2 to 6.7 kJ/m^2, which in itself offers some promise for application. Under flexural loading, the addition of fillers nonetheless resulted in a decrease in the properties, possibly due to their limited plasticity, even compared with epoxy: the loss in terms of flexural strength for the MSP6 POF4 hybrid laminate was quantified as approximately 20%. Microscopic observations also qualitatively yet consistently demonstrated good interfacial adhesion between the filler and the matrix, without significant pull-out or agglomeration, particularly in the hybrid composites. The fabrication of demonstration panels confirmed the materials' good processability, with satisfactory consolidation and predictable post-curing behavior in terms of density and dimensional shrinkage. These results may suggest that the developed composites, with obvious limitations in terms of amount of filler, could represent a promising solution for applications in the nautical sector, while also contributing to the valorization of marine waste as secondary raw materials. Two questions remain on the floor, however, such as the control of fabrication at higher thicknesses and the introduction of a larger quantity of filler, which might suggest the application of a sizing process on the *Posidonia oceanica* fibers to regularize their geometry, while at the same time preventing their agglomeration.

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Abbreviations

The following abbreviations are used in this manuscript:

ASTM	American Society for Testing and Materials
CCR	Clear Casting Resin
CCF	Clear Casting Fast
MS	Mussel Shells
MSP	Mussel Shell Powder

xMSP–yPOF	Hybrid composite with x wt.% mussel shell powder and y wt.% *Posidonia* fibers
NE	Neat epoxy (unfilled bio-epoxy resin)
PO	*Posidonia oceanica*
POF	*Posidonia oceanica* Fibers
SEM	Scanning Electron Microscopy
Vi, Vf	Initial, final volume
wt.%	Weight percentage

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