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Use of Adriatic Sea marine originated material in biocomposites with epoxy resin

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ABSTRACT

The introduction of different types of marine originated material (namely, different types of mollusc shell powders, such as mussels, oysters, and clams, and *Posidonia oceanica* fibers), originated from the Adriatic Sea, into usable materials has been proposed. The modification of the characteristics of epoxy resin obtained following the filling operation has been suggested to be representative of the respective potential and criticalities in using these materials as secondary raw materials in the polymer composites context. To obtain this preliminary information, morphological and mechanical (three-point flexure) and technological (Shore D hardness) evaluation was carried out, which provided data on the possible improvement of the production process, which might lead to their successful application, more specifically in a context linked to the nautical industry.

Keywords: composites, sea-derived materials, mollusc shell powders, mechanical properties

INTRODUCTION

Epoxy resins, for their relative reliability in terms of performance and repeatable molding, represent a suitable container for the inclusion of waste with the idea to improve their sustainability together with reducing resource depletion (Thomas *et al*., 2014). As a matter of fact, the variety of fillers employed into an epoxy resin is very large, including biofillers, ceramic, carbon and even metallic ones to offer differentiated properties to the polymer (Gonçalves *et al*., 2022). Combining this widely perceived need with the large availability of waste suitable to the purpose of resin filling offers a significant potential for the development of less expensive while more mechanically performant resins (Liu *et al*., 2014). In this regard, the geometry of the fillers plays an essential role (Tee *et al*., 2022). In the case of biofiller, the underlying idea is to proceed soon with the application of bio-based epoxies, which are increasingly receiving attention in various sectors, especially in blends with petrochemical resins (Capretti *et al*., 2023). Having in mind materials of marine origin, some interest has been reported already for their introduction into polymer resins, both for organic (cellulosic) and inorganic (ceramic) fillers (Santulli *et al*., 2023). More specifically, algae have often been considered as the raw material for composites' matrix, in the form of alginate, which has an interest in the biomedical field (Raus *et al*., 2021), into fiberglass production as a bio-epoxy (Apostolidis *et al*., 2024), or as a potential filler in various forms into other matrices, such as polylactic acid (PLA) (Bulota *et al*., 2015). In a similar way, although in much less organized way, also residues from *Posidonia oceanica* egagropila have been considered for use in materials in a blended use as a type of lignocellulosic fibers (Khiari & Belgacem, 2017) or as such for erosion control materials (Restaino *et al*., 2023). Marine originated materials can also provide large amounts of biogenic calcium carbonate, mainly from mollusc shells, which does represent a valuable substitution for quarry-extracted limestone (Piras *et al*., 2024). This practice is likely to be further expanded by the growing success of aquaculture, where the perception of seashells waste as a potentially valuable biomaterial rather than an issue has become consolidated (Morris *et al*., 2019). This involved also some potential use of seashell powders as fillers in composites, even combined with waste plastics to enhance the stiffness and abrasion resistance of the obtained materials (Balan *et al*., 2020).

This work concentrates on the introduction of seashell powders of different species and *Posidonia oceanica* short fibers coming from the Adriatic Sea as the filler for an epoxy resin. Attention is paid to their compatibility with the resin and to the potential scaling up of this process.

MATERIALS AND METHODS

Calcareous exoskeletons from mussels (*Mytilus galloprovincialis* Lamarck, 1819), oysters (*Ostrea edulis* Linnaeus, 1758), and clams (*Ruditapes decussatus* Linnaeus, 1758), originated from the Adriatic sea, have been collected, thoroughly washed and cleaned from their protein remains, and ground down using a jaw mill, then sieved to a size between 63 and 200 microns, as reported in Figure 1. *Posidonia oceanica* fibers obtained from egagropila, collected from the Boka Kotorska Bay (Montenegro), were washed to remove, as much as possible, silica and salt from these (Figure 2). Following this, quite aligned strands of ribbon-like fibers were obtained, which were subsequently chopped down to a 10 mm length. This dimension was deemed sufficient to prevent re-agglomeration of the fibers in globular structure when mixing with the resin.

For the purpose of composites fabrication, a commercially available epoxy resin with respective hardener was employed and it was allowed to mix with the filler using a vacuum molding procedure. To be compared with the neat epoxy resin as a reference, seven categories of samples were produced, containing respectively 5 or 10% mussel shell powder, 5 or 10% oyster shell powder, 5 or 10% clam shell powder, or 15% Posidonia fibers. Flexural tests were carried out according to the ASTM D790-17 standard (ASTM D790-17, 2017), while Shore D hardness was measured by adhering to the ASTM D2240 standard (ASTM D2240, 2021).

Figure 1. Sea shell powders (granulometry between 60 and 250 microns)

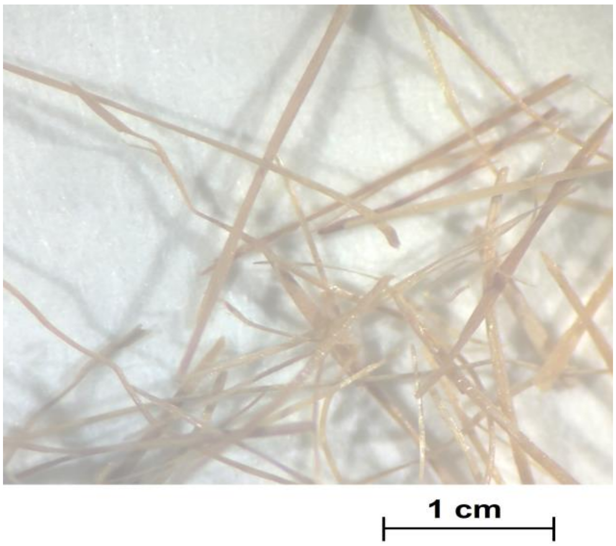


Figure 2. Posidonia fibers as extracted from egagropila

RESULTS AND DISCUSSION

It is well known that seashells are formed by calcium carbonate structures, in two different forms, namely calcite (Cal) and aragonite (Arg). However, marked differences in composition are evidenced: X-ray diffraction studies indicated the respective average percentage of calcite (Cal) and aragonite (Arg), as follows:

Mytilus galloprovincialis: 75.7% Cal, 24.3% Arg;
Ostrea edulis: 98.5% Cal, 1.5% Arg;
Ruditapes decussatus: 1.1% Cal, 98.9% Arg.

X-ray diffraction spectra, reported in Figure 3, do also indicate some presence of remaining silica into the oyster powder structure. This is likely to be more easily nested into the calcium carbonate in oyster, due to the higher complexity of its hierarchical arrangement (Barthelat *et al*., 2009).

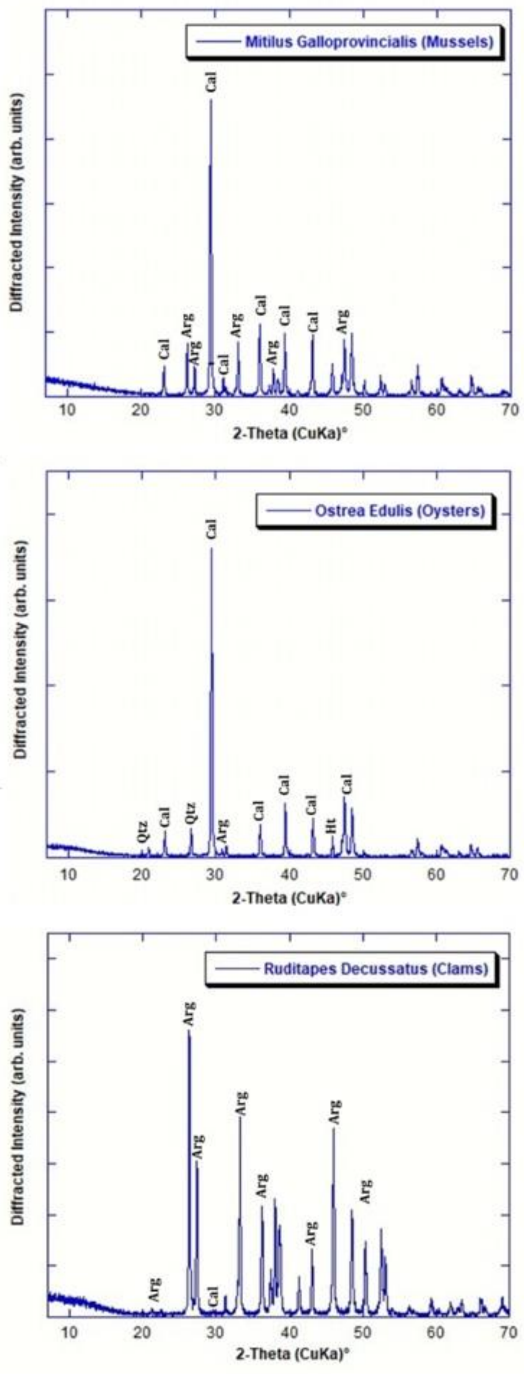
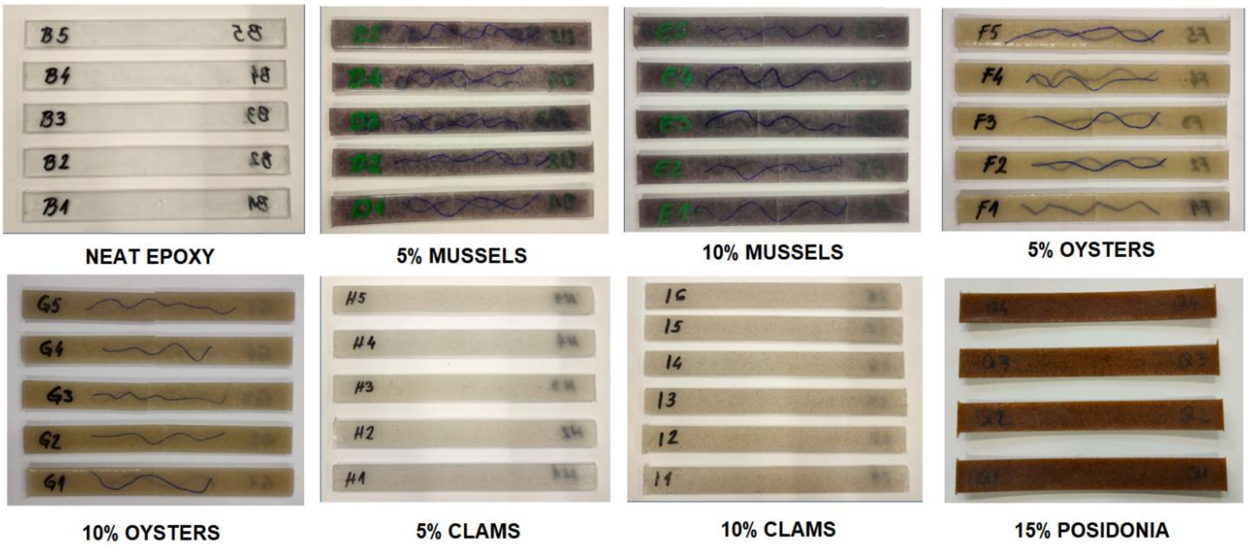


Figure 3. X-ray diffraction spectra for the different seashell powders



NEAT EPOXY

5% MUSSELS

10% MUSSELS

5% OYSTERS

10% OYSTERS

5% CLAMS

10% CLAMS

15% POSIDONIA

Figure 4. Flexural samples for the different categories of composites

The production of composite samples, which are depicted in Figure 4, including the different marine waste proved possible with some relevant caveats. More specifically, it was difficult to introduce more than 10% of seashells waste to obtain a sufficient adhesion between the resin and the filler. In the case of Posidonia, the tendency to agglomeration with resin of the fibers suggested to perform an introduction of a minimum amount of 15% of fibers. This characteristics of Posidonia is well known, and is even considered positive in some studies, which suggest the disposal of egagropila remains into the production of "green energy" (Petrounias *et al.*, 2023). For the production of materials using Posidonia, which is considered more suitable for its sustainable use in durable products, agglomeration of extracted fibers does represent an open issue (Balata & Tola, 2018). Even in this case, the distribution of the filler did not look totally uniform, as it is observed in Figure 5.

The results of flexural tests (flexural strength in Figure 6, and deflection to fracture in Figure 7) indicate that the highest performance is obtained in the case of the introduction of mussels' powder, slightly better with 5% than 10% mussels of it. Not all the samples improved the performance of the pure resin, but the scattering of properties observed in neat epoxy was always reduced by introducing the fillers. It is possible to suggest that in the case of oysters, the presence of complex fragments in the matrix, such as that reported in Figure 8, does contribute to a scarce interfacial adhesion between them and the resin, which does in turn reduce their resistance. Investigation of mussel shell structure in relation with their hardness fragmentation and their hardness has been carried out by Chakraborty *et al*. (2020). These results are basically confirmed also in our case of hardness (Figure 9), for the superiority of

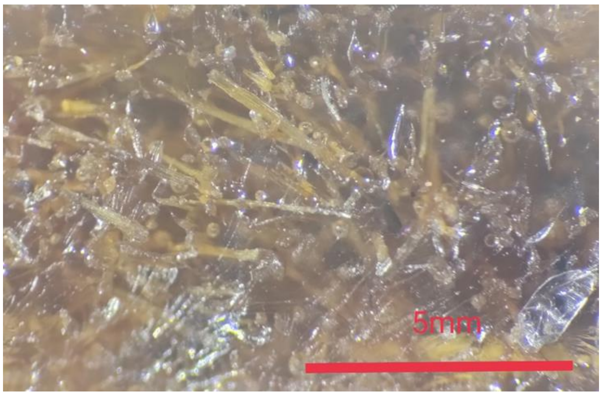


Figure 5. Posidonia fibers distribution in a relevant sample

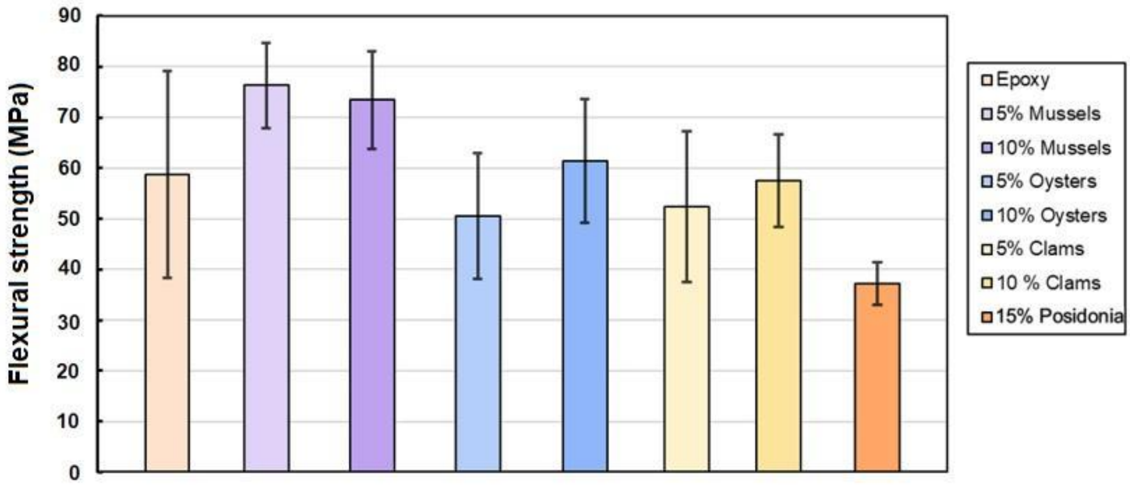


Figure 6. Flexural strength for the different categories of samples (average and standard deviation)

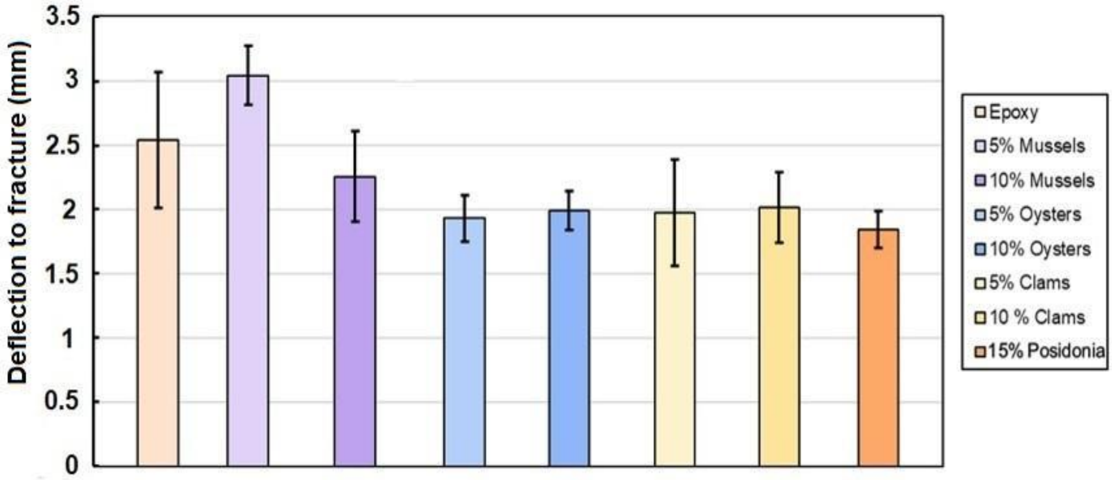


Figure 7**.** Deflection to fracture for the different categories of samples (average and standard deviation)

mussel-filled samples, where however even an introduction of 10% of these produces further improvement of this surface-based property. Some indications have been recently reported about toughened resin joints with mussel powder (Velayutham *et al*., 2024).

In Figure 10, optical microscopies of all the categories of samples are reported. Some considerations are evident from these observations, namely the fact that the fillers are upsetting the molding of the resin. The presence of bubbles is even larger and more evident for the filled samples than for the bare resin. In the case of Posidonia filled ones, the adhesion along the fiber length does not appear very uniform, also for the complex microfibrillar nature of the material.

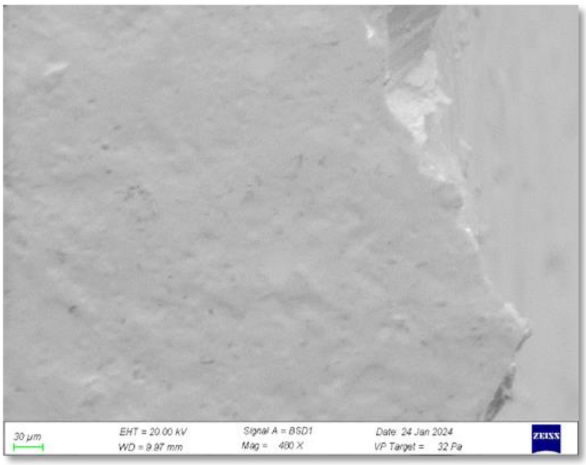


Figure 8. Fracture of a flexural sample containing oyster shell powder due to cracking of the particle

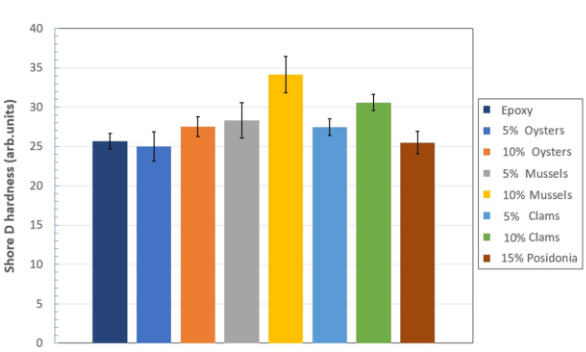


Figure 9. Shore D hardness for the different categories of samples (average and standard deviation)

CONCLUSIONS

The results of this study show that a tentative introduction of sea-originated materials, such as mollusc shells powder, and Posidonia fibers, is possible in small amounts and might even improve the properties of the resin filler.

As regards oysters, mussels and clams powder, a dependence from their biological structure is observed in the final characteristics of the materials obtained. Some limitations are further highlighted, that for this procedure to possibly have some further development in the future, the production process needs to be modified to reduce the penetration of air in the material.

These improvements will be needed in order to apply a resin more dedicated to the use in the nautical field, which will offer a wider sense to this operation, and possibly with some bio-based content, to reduce the environmental impact of the process.

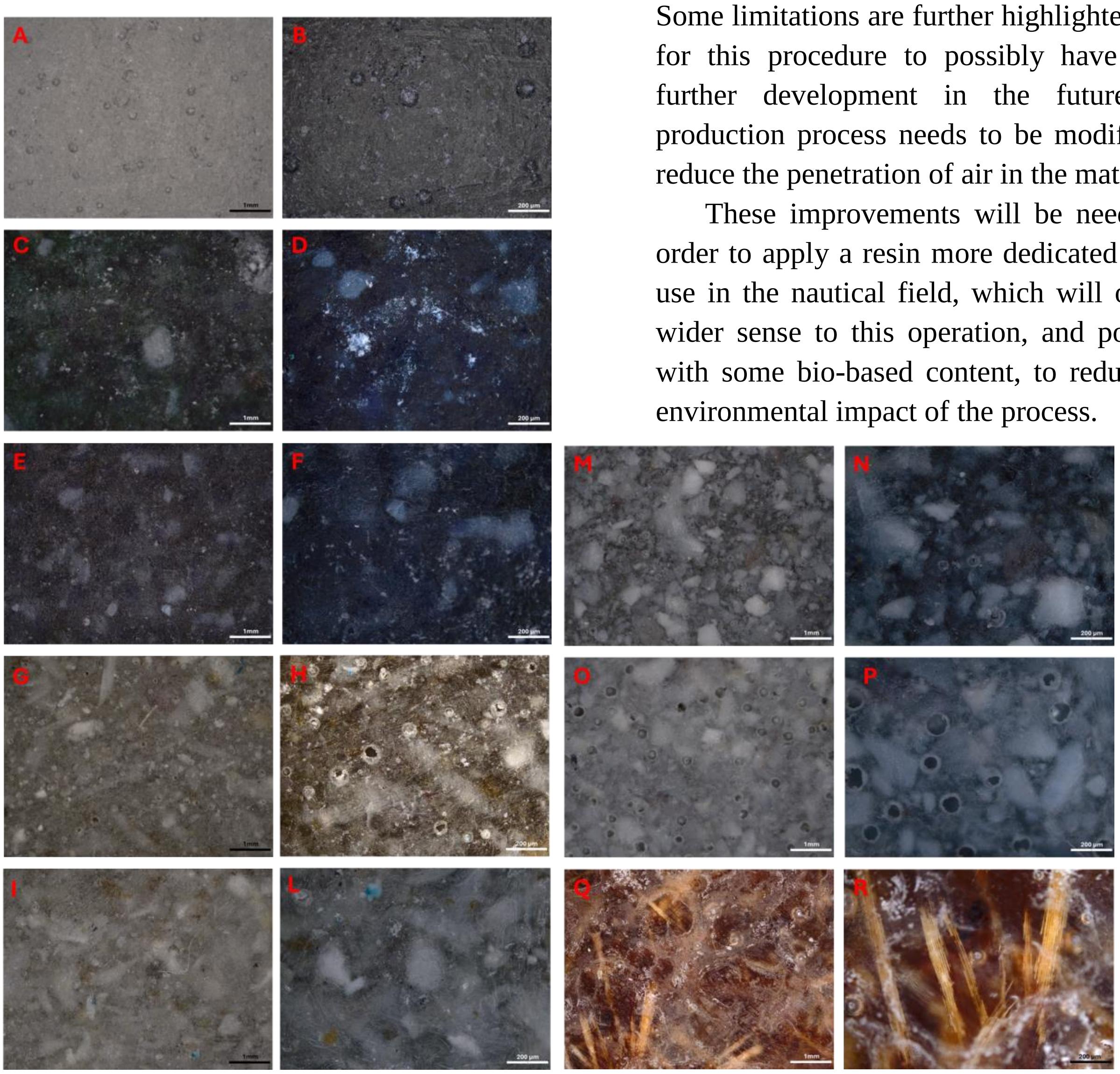


Figure 10. Optical Microscopy of various composite samples: A. and B. epoxy; C. and D. epoxy with 5% mussels' powder; E. and F. epoxy with 10% mussels' powder; G. and H. epoxy with 5% oysters powder; I. and L. epoxy with 10% oysters' powder; M. and N. epoxy with 5% clams powder; O. and P. epoxy with 10% clams powder; Q. and R. epoxy with 15% Posidonia fibers. Scales are: 1 mm for A., C., E., G., I., M., O. and Q.; 200 microns for B., D., F., H., L., N., P. and R.

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Upotreba materijala iz Jadranskog mora u biokompozitima s epoksidnom smolom

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SAŽETAK

Predloženo je uvođenje različitih vrsta materijala iz Jadranskog mora (zapravo različitih vrsta praha od školjki mekušaca kao što su mušulje, ostrige, vongole i vlakna Posidonia oceanica) u upotrebljive materijale. Modifikacija karakteristika epoksidne smole dobijene nakon procesa kombinovanja s ovim materijalima predstavlja odgovarajući potencijal i kritičnost u korišćenju ovih materijala kao sekundarnih sirovina u kontekstu polimernih kompozita. Da bi se dobile ove preliminarne informacije, izvršena su ispitivanja: morfološka i mehanička (savijanje u tri tačke) i tehnološka (tvrdoća po Shore D), čime su dobijeni podaci o mogućem poboljšanju procesa proizvodnje, što bi moglo dovesti do njihove uspješne primjene, tačnije u kontekstu nautičke industrije.

Ključne riječi: kompozitni materijali, materijali iz mora, prah školjki mekušaca, mehanička svojstva