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Conservation of Underwater Cultural Heritage: preliminary coatings testing within the TECTONIC project

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Abstract **– Underwater Cultural Heritage (UCH) encompasses all traces of human existence found beneath the water's surface, such as shipwrecks, submerged structures, and various archaeological sites. Preserving UCH presents numerous challenges due to the distinctive environmental conditions, difficulties associated with accessing and working in underwater environments, and the potential risks posed by natural forces and human activities. The TECTONIC project aims to foster collaboration between academic and non-academic professionals, facilitating the exchange of skills and expertise. The project's objective is to implement, enhance, and evaluate innovative materials, techniques, tools, and methodologies for the protection of Underwater Cultural Heritage. Within this context, the University of Calabria (Italy) and Synpo akciova spolecnost (Czech Republic) are collaborating on technology and scientific exchanges to develop an underwater coating with antifouling properties suitable for safeguarding underwater cultural heritage.**

I. INTRODUCTION

Underwater Cultural Heritage (UCH) encompasses a vast and enigmatic realm of human history, offering a unique perspective into the depths of our shared past. From shipwrecks that tell tales of maritime exploration to submerged cities that unveil ancient civilizations, UCH provides a tangible link to the cultures and societies that once thrived along the world's coastlines and waterways. However, the submerged past is not invulnerable; it is subject to a range of degradation phenomena that challenge our ability to preserve and protect this invaluable heritage.

In recent years, there has been an increasing interest in the study of degradation phenomena that occur at archaeological sites located underwater. Numerous research endeavors have focused on examining the deterioration of stone materials in underwater environments and developing innovative strategies to safeguard them [1-12].

Natural processes play a significant role in the degradation of UCH. Underwater sites are subject to relentless natural erosion, which occurs as a result of water currents, wave action, and the abrasive force of sediments carried by the sea. Over time, these forces can wear away at submerged structures and artifacts, slowly erasing the intricate details and historical context they contain. This process is particularly pronounced in dynamic underwater environments, where the constant movement of water can exacerbate the effects of erosion. As a result, the remnants of once-majestic vessels and coastal settlements may gradually succumb to the relentless embrace of the ocean, fading into obscurity.

Furthermore, one of the most significant forms of damage to submerged archaeological artifacts is the colonization by organisms (bio-fouling). This phenomenon occurs rapidly, within a few hours of material surfaces being exposed to natural marine environments. Over extended periods of exposure, marine fouling takes the form of a diverse community of plants, animals, and microorganisms, leading to substantial alterations and influences on the immediate environment surrounding the stone surface. It is important to note that the accumulation of biofouling and biofilm formation is not uniformly distributed in time and space, but rather a complex process. [7, 10, 13, 14].

In the face of these degradation phenomena, a multifaceted approach to safeguarding UCH has emerged. The most recent guidelines issued by scientific and international organizations dedicated to the protection of cultural heritage endorse the promotion, safeguarding, and preservation of underwater archaeological and historical sites. These guidelines align with the principles outlined in the UNESCO Convention on the Protection of the Underwater Cultural Heritage, ratified on November 2nd, 2001 [15]. The present research, developed in the framework of the TECTONIC project (EU-H2020-MSCA-RISE-2019-873132-TECTONIC TEchnological Consortium TO develop sustaiNabIlity of underwater Cultural heritage), aims to develop an epoxy resin-based system with antifouling properties for the conservation and preservation of underwater stone materials. The TECTONIC project, focused on safeguarding underwater cultural heritage (UCH), introduces innovative strategies. It emphasizes advanced monitoring techniques using remote sensing, underwater drones, and sonar mapping to assess UCH site conditions in real time. International cooperation is promoted to address global UCH preservation collectively, recognizing its shared significance. Additionally, the project emphasizes public education and community involvement to create awareness and discourage illegal activities. These comprehensive strategies aim to protect UCH, ensuring its accessibility, and enriching our understanding of maritime history for future generations [16].

The work is still in progress and therefore only the preliminary results based on the initial stages of laboratory experimentation will be discussed in the next paragraphs.

II. MATERIALS AND METHODS

The first step of the research focused on a screening of the various epoxy resin-based systems produced by Synpo doped with anti-fouling additives, trying to find out the most suitable and compatible formulation for underwater application [17-19]. Colorimetric tests, contact angle measurements, capillarity water absorption test, scotch tape test, color variation after UV aging, and underwater applicability were therefore evaluated, while the antifouling and ecotoxicity tests are still in progress. The products were applied on marble and limestone specimens sized 5x5x2 cm, in order to evaluate any different performance of the coatings on the most commonly lithotypes used in the field of cultural heritage [20, 21].

The chosen products are in particular: a two-layers resin-based mixture (AG version for marble, AM version for limestone), and a mono-layer resin-based system doped with two different anti-fouling additives (EQ and EZ). Due to a patent application, further information about the products will be available only on request.

Color variations induced by the treatment were evaluated by means of colorimetric tests [22], using a CM-2600d Konica Minolta spectrophotometer. Chromatic values are expressed in the CIE L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue).

Contact angle measurements [23] was carried out in order to determine the wettability of the treated surface, as this parameter may influence the adhesion of micro-organisms in the underwater environment. The measurement consisted in the placement of a water drop of defined volume on the solid sample surface. Drop shape was recorded with a camera and automatically evaluated in terms of contact angle. The average value of 5 drops determines the contact angle.

Scotch tape test [24] was used to assess the superficial cohesion of the stone before and after the treatment. Test consists in the application and removal of tape by hand for five times on the same surface.

Absorption tests were carried out before and after the treatment in order to determine the variation of stone porosity after application of the coating. The absorption test was performed following UNI 10859:2000 - Determination of water absorption by capillarity [25]. It consists of measuring the amount of water absorbed by capillarity from the specimens per unit area, as a function of time. The test was performed on triads of specimens, one per type of treatment, untreated included. The specimens are placed with the treated surface in contact with a layer of filter paper sheets (1cm thick) saturated with deionized water. Measurements are taken at nonlinear time intervals (referred to the start of the test: 10min, 20min, 30min, 1h, 4h, 6h, 24h…) according to the formula (1)

$$Q_i = (m_i - m_0)*1000/A \qquad (1)$$

where:
Q_i = capillary absorption coefficient (g/cm^2),
A = specimen surface in contact with filter paper layer (cm^2);
m_i = wet specimen mass (g) at t_i (s$^{1/2}$);
m_0= dried specimen mass (g).

Artificial accelerated aging test for simulation of solar radiation was performed using a SUNTEST XLS+ (Atlas, USA) in order to evaluate the stability of the coating, as resins are susceptible to UV degradation. Test lasted for 500 hours, simulating one year outdoor exposure [26].

The suitability for underwater application was assessed by utilizing standardized two-component cartridges equipped with a static mixer. This ensured the proper mixing of the components without the presence of water. The pre-mixed coating was subsequently applied using different tools such as a brush, sponge, or spatula in an aquarium. It is worth noting that for the underwater tests, the original formulation was adjusted by incorporating a UV-sensitive pigment. This modification aimed to verify the effectiveness of the product application. Importantly, the inclusion of this pigment did not have any impact on the final thermo-mechanical properties of the product.

III. RESULTS AND DISCUSSIONS

Colorimetric measurements pointed out negligible color variation both after treatment and aging for all the samples (Table 1, 2). Color variations are imperceptible to human eye when ΔE<5.

Table 1. Color variations after coating application on limestone specimens and aging.

Samples	ΔE (Treated–untreated)	ΔE (Aged–untreated)
AM	3.1	3.5
E	1.8	2.0
EQ	2.8	3.7
EZ	2.2	2.9

Table 2. Color variations after coating application on marble specimens and aging.

Samples	ΔE (Treated–untreated)	ΔE (Aged–untreated)
AG	1.5	1.7
E	0.2	0.3
EQ	3.2	3.8
EZ	2.0	2.4

Contact angle measurements highlighted an increase in hydrophobicity on both limestone (0° untreated) (Table 3) and marble (32°) (Table 4) in almost all cases; the increase in hydrophobicity is minimal for EQ treatment on marble.

Table 3. Contact angle measurements after treatment and after aging test on limestone samples.

Samples	Contact angle (◦) after treatment	Contact angle (◦) after aging
AM	88±10	85±7
E	69±4	68±3
EQ	35±4	33±2
EZ	63±3	61±2

Table 4. Contact angle measurements after treatment and after aging test on marble samples.

Samples	Contact angle (◦) after treatment	Contact angle (◦) after aging
AG	98±2	94±1
E	69±5	66±5
EQ	68±5	62±6
EZ	64±5	63±3

Concerning the scotch tape test, marble samples had a great superficial cohesion, showing a zero loss of material in both the treated and untreated cases. For limestone samples it's possible to observe an increase of superficial cohesion after treatment (Fig.1).

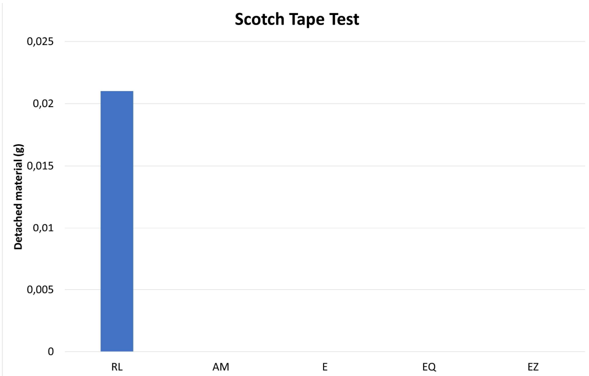

Fig. 1. Superficial adhesion evaluation by scotch tape test on limestone samples.

Absorption test on limestone specimens showed a decrease in absorption capacity after treatment (Fig. 2).

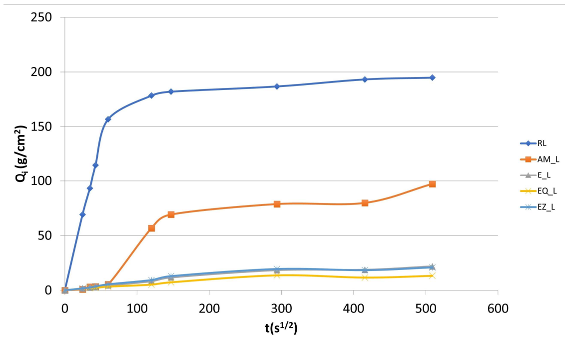

Fig. 2. Capillary water absorption on limestone specimens.

On marble specimens instead, due to the low absorption capacity of the natural stone itself, there are no marked differences between untreated and treated samples (Fig 3).

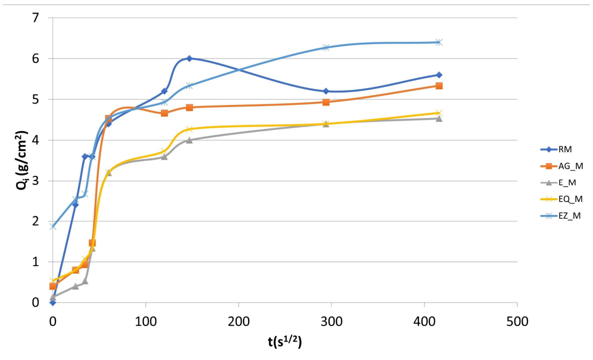

Fig. 3. Capillary water absorption on marble specimens.

The underwater applicability tests focused on several aspects: possible dispersion of the product during application, ease of application depending on the tool used, and hardening of the product. Products showed a good applicability in the underwater environment, using soft brushes and/or sponges (Fig. 4), even though issues with short pot life of the mixed product emerged.

Fig. 4. Different application methods on limestones. W=wet samples, on air application; UW=underwater application; BR=brush, SPT=spatula, TB=toothbrush, SPU=PVA sponge, SPG=sponge.

IV. CONCLUSIONS

The research carried out in the frame of the TECTONIC project is still in progress, but the preliminary results are well promising. Treatments had improved the mechanical properties of the samples, such as surface adhesion strength, hydrophobicity, and a reduced interconnected porosity, without altering the color. Moreover, erosion phenomena and growth of microorganism should be, hopefully, discouraged. From applicability point of view, results are encouraging: it was possible to apply the products with several tools obtaining a homogeneous layer; the only downside was the short pot life of some products but it will be addressed in the next phases of experimentation. The next stages of laboratory research will focus on antifouling tests on the already formulated products in order to guarantee their safe use for the protection of underwater objects and stone materials of cultural interest. Moreover, the experimentation will move to its final part, applying coatings in underwater pilot sites chosen in the frame of the project.

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