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COMPOSITE MATERIAL WITH ANTIMICROBIAL EFFECT FOR THE PRESERVATION OF WATERLOGGED WOOD CULTURAL HERITAGE OBJECTS

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The underwater cultural heritage represents an important component of the cultural heritage which does not represent a preferred research topic due to the degree of difficulty posed by the objects that constitute it (furniture, ships). To solve this problem, we propose the synthesis of a nanocomposite material to treat waterlogged wood. This material is composed of an apatitic material (with antimicrobial role) and a polymeric compound (with filling role and designed to improve the mechanical properties). The composite was characterized morpho-structurally and successfully applied to the most common types of wood (ash, pine, oak, fir)

Keywords: cultural heritage, waterlogged wood, apatitic materials, nanomaterials, consolidation, archaeological wood

1. Introduction

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Cultural heritage can be seen as the mark humanity has left on the planet from its inception to the present day. One of the most recognized roles of cultural heritage is its historical significance, as it serves as an ongoing source of knowledge and learning. Additionally, cultural heritage holds special economic importance. Many countries experience substantial economic growth by leveraging their heritage for tourism and addressing the conservation challenges it presents. This, in turn, spurs the advancement of various scientific fields as new materials are developed to preserve it. For instance, Greece's economy heavily depends on tourism, capitalizing on its rich cultural heritage. Similarly, Italy not only benefits from tourism but has also fostered a research sector focused on developing and commercializing new conservation materials [1].

In recent decades, the concept of cultural heritage has broadened and is now divided into two main categories: tangible and intangible cultural heritage. Tangible heritage include immovable heritage (architectural structures, monuments, buildings and historical sites), movable heritage (objects and artefacts such as works of art, instruments, documents and tools), natural heritage (landscapes, biodiversity and natural features that have a cultural meaning), while intangible heritage includes traditions and rituals (practices, ceremonies, festivals and customary rituals), the various forms of expression (music, dance, theater and other forms of artistic expression), oral traditions (folklore, stories, myths and languages), knowledge and skills (traditional crafts, techniques and skills passed down through generations) [2].

Wood is one of the organic materials most used by humans, since ancient times. By processing it, people at first built the things they needed in everyday life such as shelter with a residential or religious role (churches), tools used in agriculture or hunting, ships to move at sea or for fishing. Along with the evolution of humanity, they managed to take wood processing to the level of art, to manufacture simple or sophisticated furniture items, sculptures, musical instruments, or objects used in rituals [3]. Wood mostly consists of 3 components: cellulose, hemicellulose and lignin. Like any organic material, after it is cut, in the presence of water, oxygen and different bacteria or fungi, it degrades. Wood is divided into two categories, hardwood (maple, beech, ash, walnut, oak, etc.) and softwood (spruce, fir, cedar, pine, etc.) [4].

Waterlogged wood refers to wood that has been saturated or soaked with water for an extended period of time. This saturation occurs when the wood is immersed in water or exposed to a constant high level of humidity and the water penetrates its entire structure, down to the smallest level (capillarity, microcapillarity) and it reaches its saturation point [5].

Normal wood and waterlogged wood differ primarily in their exposure to water and the subsequent changes that occur in their physical and chemical properties. The main characteristics that change are moisture content, density, strength, color, and degree of disintegration. Understanding these differences is crucial for researchers, conservators and historians working with waterlogged wood, in order to ensure proper preservation and development of materials used for this purpose.

Waterlogged wood has several distinctive features, under some particular conditions being observed improvements of its various physical or chemical properties, compared to normal wood. One of the positive aspects is represented by improved resistance to rot, due to the fact that saturation limits the amount of oxygen available, slowing down the activities of fungi and bacteria that usually contribute to wood decay. Another positive aspect of water-immersed wood is its preservation, as waterlogged wood can be well preserved for long periods, especially in anaerobic environments. This has archaeological significance, as artifacts and wooden structures can be found in a relatively intact state in underwater or waterlogged archaeological sites. The main problem in this type of preservation is represented by bringing them to the surface. Once removed from the aquatic environment, their structure is full of pores and cracks caused by water, and oxygen and bacteria can quickly penetrate, causing irreparable damage in a relatively short time [6,7].

In the last decades, a fairly good solution for the preservation and conservation of cultural heritage was represented by phosphate compounds, more precisely apatitic materials. As a spread, this can be obtained both from natural sources (soil, bones) and as a synthetic product. Their synthesis is simple, without obtaining many secondary compounds, cheap and easy to apply. Hydroxyapatite is a calcium phosphate with a great ability to accept numerous cationic or anionic substituents. Depending on the final purpose, the reaction parameters can be modified so that hydroxyapatite is used in many fields such as conservation of cultural heritage, biosensors, medicine; in addition, it has been observed that it can be doped with heavy metals, thus increasing the properties and acquiring antimicrobial action [8,9].

To serve the intended purpose of the apatitic materials, they must be held in close contact with the surface of the wooden object that is to be protected. For this reason, the particles must be embedded in a polymeric matrix (binder) that serves the purpose of keeping the microorganisms-inhibiting apatitic materials in an impermeable thin film, ensuring proximity of the particles to the wooden surface even when harsh external factors are present, such as intense UV radiation (from sunlight), high humiditiy, oxidizing environments, abrasion and impact damage, mechanical stresses caused by shrinking and swelling of wood according to its moisture content [10], thermal expansion and contraction, etc.

In the same time, the resulting composite coating, formed by embedding the apatitic filler in the polymeric matrix, must have a minimal impact towards the aesthetics of the wooden samples. In this regard, the coatings must be transparent, even when much higher concentrations than the minimum inhibitory concentrations of opaque apatites are used.

Polyurethane is an excellent choice for this purpose due to its advantages over other binders such as alkyd, acryl or epoxy[11]. First advantage would be that polyurethane is a highly versatile polymer, and its thermo-mechanical properties can be fine-tuned according to the necessities, by varying the ratio of soft segments/hard segments or by crosslinking[12]. Secondly, polyurethane is a polymer that is resistant to the degradation done by solvents and chemicals[13], UV radiation (photolysis)[14], water (hydrolysis) (for ether-based polyurethane)[15], microorganisms (biodegradation)[16]. Thirdly, as a binder used in coatings, polyurethane displays very good adhesion to many substrates[17]. More than that, the polyols used in the polyurethane synthesis along with the diisocyanate can readily be synthesized from renewable resources such as vegetable oils, through simple reactions such as epoxide ring-opening reaction[18] among others or from lignocellulosic biomass[19]

As an environmentally-friendly alternative to oil-based polyols, polyols can also be synthesized by the glycolytic depolimerization of polymers such as polyesters[20], polyurethanes[21] or polyamides[22].

An ubiquitous high volume polyester that is not readily biodegradable[23], in normal conditions, is polyethylene therephthalate. This polymer is one of the most produced plastics, ranking 7th by volume in Europe, in 2021[24]. For these reasons, it is imperative to find new uses of the products resulted from PET glycolysis, in an attempt to upcycle the waste plastics into high performance and high-quality materials that can be used for particular, high-demanding applications.

To solve this problem, the present study proposes the development of a composite material that closes the pores, fills the cracks and forms a protective layer against oxygen, bacteria and fungi on the waterlogged wood. The material is made up of an antimicrobial component (apatite material) to protect the wood against fungi and bacteria and a polymer with the role of filling, strengthening and increasing mechanical resistance [25].

2. Experimental

2.1. Materials and methods

The compounds necessary for the synthesis of hydroxyapatite ($Ca(NO_3)_2$, $(NH_4)_2HPO_4$, $CoCl_2$ and $ZnCl_2$) were purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany) and the solvents used in the reaction (ammonia, ethanol) from Chimreactiv SRL (Bucharest, Romania). The substances used for the aging of the wood, $Na_2S \cdot 9H_2O$, and $FeCl_2 \cdot 4H_2O$ were purchased from Merck KGaA (Darmstadt, Germany), and Thermo Fisher Scientific (Waltham, Massachusetts, USA), respectively. For the development of the polyurethane-based binder were used the following reagents: the experimental **polyol RC3r** was obtained in our laboratory by glycolytic depolymerization of polyethylene therephthalate in a method described by Duldner et. al.**[**26**]**, slightly modified. The resulted liquid polyol had a hydroxyl index of 71.4 mg KOH/g and an acid value of 4.54 mg KOH/g, determined using the methods specified in ASTM-D4274-21 and ASTM D4662-20 technical standards, respectively**,** and a dynamic viscosity of 1538 cP at 25 °C. **Castor oil (C.O.)** was purchased from TIS Farmaceutical (Bucharest, Romania), **anhydrous glycerol (Gly)** was obtained from Chimopar S.A. (Bucharest, Romania), **isophorone diisocyanate (IPDI)** 98%, mixture of isomers, was obtained from Sigma Aldrich (Saint Louis, Missouri, USA); **dibutyltin dilaurate (DBTDL)** was obtained from Merck Schuchardt OHG (Hohenbrunn, Germany), defoamer additive for polyurethane systems **BYK-1796®**, dispersing additive **Disperbyk-180®** and surface additive **BYK-333®** were obtained from BYK Additives & Instruments (Wesel, Germany), while **N-butyl acetate** and **Acetone** were obtained from Chimopar S.A. (Bucharest, Romania).

2.2. Synthesis and characterization

The synthesis of the apatite materials was carried out by the co-precipitation method [27], starting from obtaining a solution in which calcium nitrate ($Ca(NO_3)_2$) and metal chloride (Zn or Co) were dissolved, in different molar ratios (as presented in Table 1), distilled water being used as solvent. The reaction proceeds under continuous heating and stirring. When the solution reaches 80°C, a solution consisting of diammonium phosphate ($(NH_4)_2HPO_4$) dissolved in water is added dropwise; after complete addition of the phosphate solution, the reaction is continued for 3 hours at constant temperature and pH=10. After the reaction stops, the compound is washed with water under vacuum, to remove excess ammonia, until the pH is neutral, then it is mixed with ethanol until a gel is formed and dried in a vacuum oven. Apatitic material is obtained in the form of powder in which calcium has been displaced with Zn or Co. The table below shows the abbreviations of the synthesized materials:

Table 1

Abbreviations for the synthesized materials

Synthesized material	Abbreviation
Hydroxyapatite substituted with Zn, Ca:Zn molar ratio 1:1	HAP-Zn 1:1
Hydroxyapatite substituted with Zn, Ca:Co molar ratio 3:1	HAP-Co 3:1

The synthesis of a polymeric binder film, without the addition of apatite, was achieved by the polyaddition reaction in solution between a mixture of environmentally friendly polyols (polyol RC3r, glycerol and castor oil) and IPDI.

The reaction took place in acetone while DBTDL, used as a catalyst, and BYK-1796® antifoaming additive were also added to improve the curing time and the film appearance and integrity. In this regard, the polyol mixture was chosen to be composed of 5% Castor oil, 20% glycerol and 75% polyol RC3r by weight. The IPDI amount was calculated in relation with the polyols so that the NCO/OH ratio would be 1.1. The amounts of DBTDL, used as a catalyst, and the additive BYK-1796® were each calculated to be 0.5 wt% of the mass of the binder (mass of IPDI plus the mass of the polyols). The amount of solvent (acetone) used was equivalent (100 wt%) to the binder mass.

For a typical synthesis, the three polyols were weighed in a plastic (polypropylene) cup. Then, the DBTDL and the BYK-1796 were added, followed by lightly stirring the mixture with a spatula. Then, the IPDI and and the acetone were added, followed by vigorous stirring on a magnetic plate (at 400 RPM, for 1 hour). The resulting mixture was then cast in rectangular parallelepiped silicone mould. The silicone mould containing the polyurethane solution was left at room temperature for 24h, followed by 24h of curing in an oven, at 50°C, obtaining thin sheets of transparent, solid polyurethane.

For the composite material, the acetone used as a solvent was replaced with n-butyl acetate in order to reduce the condensation of water on the surface of the films associated with the evaporative cooling below the dew point **[28]**. The condensed water would react with the isocyanate to form CO_2 bubbles, which will impair the film integrity and thus its purpose. Also, because a colloidal system is formed by mixing the apatite powder in the liquid polymeric/solvent matrix, an additive is required in order to stabilize the sol. For this reason, we used the commercial dispersant Disperbyk-180®. The amount added was calculated as 5% of the weight of the apatite used. Lastly, in order to improve the slip and leveling characteristics of the composite film, the surface additive BYK-333® was used in ratio of 0.1% of the mass of the binder.

To verify that the apatitic material was obtained and the substitution reaction with heavy metals proceeded successfully, the materials were analyzed by X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR) analyses. Thermal analysis (AT) was used to study the thermal stability of the materials.

The polymeric film without filler was chemically characterized by FTIR, thermally by DSC and morphologically by scanning electron microscopy (SEM).

After applying the material to the different types of wood, they were morphologically characterized using SEM analysis.

The apatite compounds were analyzed by X-ray fluorescence [29] to identify the heavy metal peaks of interest and to find potential impurities. A portable XRF analyzer (Vanta C Series Handheld XRF) was used in this method. It is equipped with a 40 kV x-ray tube, rhodium anode, Silicon Drift Detector, pre-calibrated in GeoChem mode, having a 60 s acquisition time for each beam (the equipment using two different energy beams for element quantification, one for light elements - 10 kV) and one for the heavier elements - 40 kV).

FTIR characterization [30] was carried out using a Jasco FTIR 6300 spectrometer (Jasco Corporation, Tokyo, Japan) which contains a diamond crystal attenuated total reflection accessory (KRS5 lens) and the measurements were made in the 400–4000 cm^{-1} range, involving 30 scans, with 4 cm^{-1} resolution.

The thermal stability of the apatitic materials was evaluated using a Q5000IR thermogravimetric analysis (TGA) instrument (TA Instruments, New Castle, DE, USA), heating rate 10 °C/min, from room temperature to 750 °C, in platinum vessels, under a synthetic air atmosphere (99.999%), at 50 mL/min [13].

For the morphological characterization, the electronic microscopy (SEM), alongside energy dispersive X-ray spectroscopy (EDX) was used to identify the elements present in the obtained compounds. The analysis was performed using a Hitachi TM4000plus II Field Emission Scanning Electron Microscope coupled to an Energy Dispersive X-ray (EDX) spectrometer. Once the analysis begins, the samples are "bombarded" with an electron beam, which can generate charging effects at their level, thus affecting the quality of the analysis. In order to perform a thorough characterization of the materials, the following technical characteristics were taken into account: BSE detector, acceleration voltages of 5 kV, 10 kV or 15 kV and the magnification range between x100÷x100000 to get the best image quality.

The polymeric film obtained without filler was chemically characterized by FTIR spectrometry, using a Nicolet™ Summit™ Pro spectrometer, produced by Thermo Fisher Scientific Inc., USA, coupled with an Everest ATR Diamond accesory. 16 scans between 400 cm^{-1} and 4000 cm^{-1} were acquired, with a spectral resolution of 4 cm^{-1}.

DSC characterization of the sheets was performed using a Q2000 instrument produced by TA Instruments, USA, using helium as the inert gas, a temperature that ranged from -85 °C to 210 °C and the heating rate was 10 °C/min. 2 scans were acquired, in order to identify reversible and irreversible transitions.

The aesthetic effects of the treatment on the wood were made through color and gloss tests at several points. The gloss test was done with a glossmeter (PCE-GM80-ICA), equipped with an external gloss sensor, and the measurements were made on a 4.5 mm surface at an angle of 60°; the color tests were performed with a colorimeter (PCE-XXM20) equipped with an extremely sensitive RGB photodiode system as a color sensor. The measurements were made in several points and were evaluated using the L*, a*, b* coordinates of the CIE76 scale and based on these values ΔE was calculated to evaluate the potential color differences.

2.3. Antimicrobian tests

Qualitative and quantitative tests were performed to see if the apatitic materials had antimicrobial properties on gram-positive, gram-negative and fungal strains. Qualitative tests were performed by the method of minimum inhibitory concentrations on petri dishes for 24 hours and quantitative tests by the method of minimum concentrations of biofilm eradication by binary dilutions in 96-well plates.

2.4 Wood Aging

The selection of wood for aging was based on 2 criteria: according to their availability, the most common types of wood being selected, from which the heritage objects are made (fir, oak, pine, ash). A second criterion was represented by the 2 large classes of wood, namely: hardwoods (ash, oak) and resinous (fir, pine). The wood samples were cut to the same size: 6x2x1 cm (length, width, height), the only difference being registered for the pine with a thickness of 1.5 cm. For the aging of the wood, a solution was made in which $Na_2S \cdot 9H_2O$ and $FeCl_2 \cdot 4H_20$ were dissolved using water as a solvent [31]. The wood was immersed in the aging solution for about 2 days, followed by a drying process in the oven (at 40 °C).

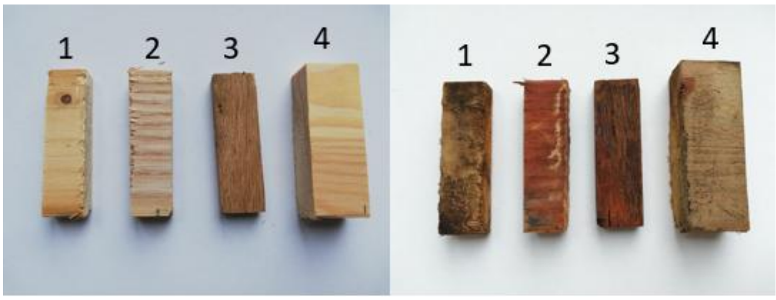


Fig. 1 Wood before (left) and after aging (right): 1 - fir, 2 - ash, 3 - oak, 4 - pine

3. Results and discussions

X-ray fluorescence characterization was performed to identify the presence of the metals of interest, to identify potential impurities and to confirm the fact that Ca substitution with heavy metal (Zn, Co) was successfully produced. From the XRF spectra shown in Fig. 2 and 3 the specific peaks (K_α, K_β) of Ca and heavy metals (Zn, Co) were identified, resulting from this the fact that the substitution took place successfully and it can also be observed that the obtained compounds do not present major impurities

In the Figs. 4-5 the FTIR spectra of classic hydroxyapatite and those substituted with heavy metals are presented. In both spectra, the peaks for the phosphate groups at 1021 cm^{-1}; 962 cm^{-1}; 559 cm^{-1} and those of the hydroxyl groups at 3244 cm^{-1} specific to hydroxyapatite can be observed.

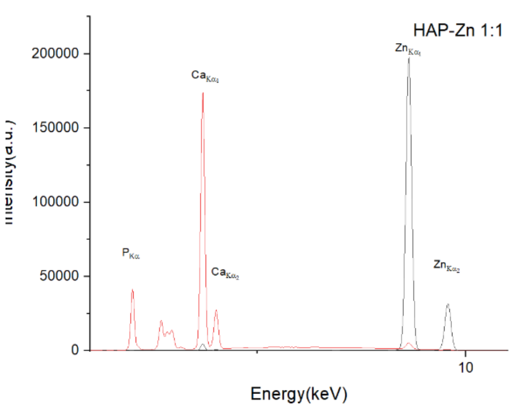


Fig. 2. X-ray fluorescence spectra of HAP-Zn 1:1.

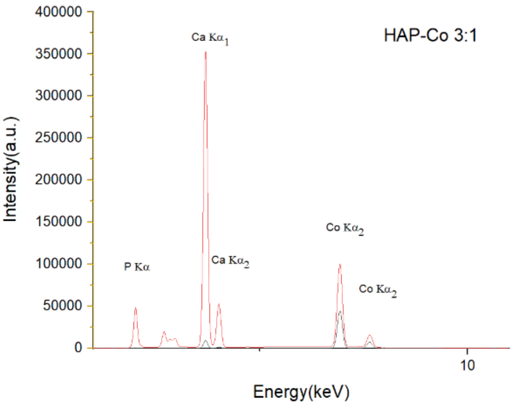


Fig. 3. X-ray fluorescence spectra of HAP-Co 3:1.

In addition, one can observe the fact that the peaks specific to the phosphate group from 559 cm^{-1} and 600 cm^{-1} are slightly shifted to the left at 619 cm^{-1} and 556 cm^{-1} specific to the bonds formed between oxygen and Zn/Co.

Thermogravimetric analyzes were performed to observe if the compounds are thermally stable. As it can be seen from Figs. 6-7 they present a residue of approximately 87.25% for HAP-Co and 75.82% for HAP-Zn. Mass losses for compounds take place in three stages: in the first stage (room temperature - 120°C) the desorption of water takes place in which HAP-Co loses approximately 8.06% of its mass and HAP-Zn 0.52%. The second stage, HAP-Co (120-300°C) shows a relatively low mass loss of 2.74% compared to that of HAP-Zn (120-410°C) which loses approximately 21.24% of mass, associated with the loss of water from the network. In the last stage (up to 1000°C), relatively similar mass losses occur in both cases, 1.95% for HAP-Co and 2.44% for HAP-Zn associated with the dehydroxylation of apatitic materials.

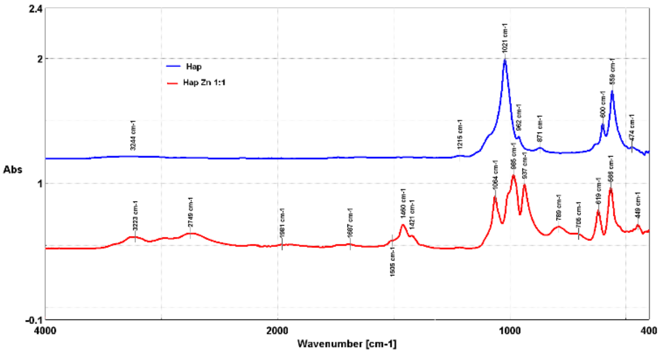


Fig. 4. FTIR spectrum of classic hydroxyapatite compared with the spectrum corresponding to hydroxyapatite substituted with Zn

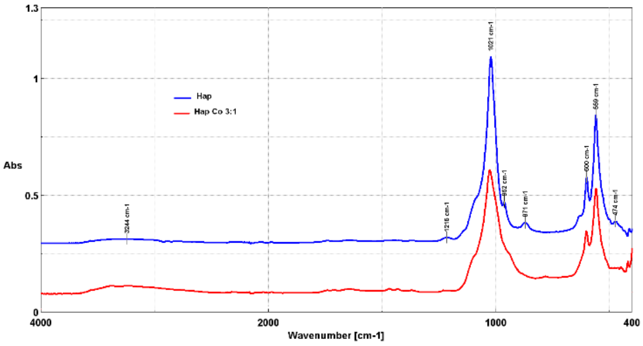


Fig. 5. FTIR spectrum of classic hydroxyapatite compared with the spectrum corresponding to hydroxyapatite substituted with Co

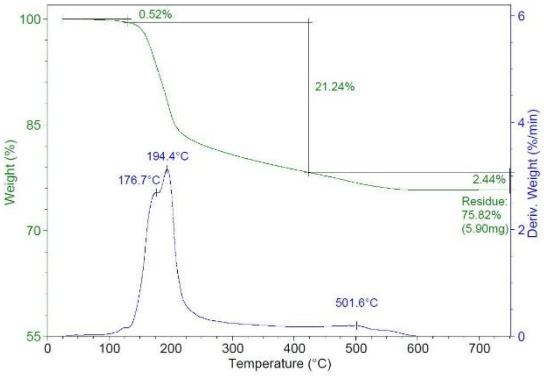


Fig. 6. Thermogram of hydroxyapatite substituted with Zn.

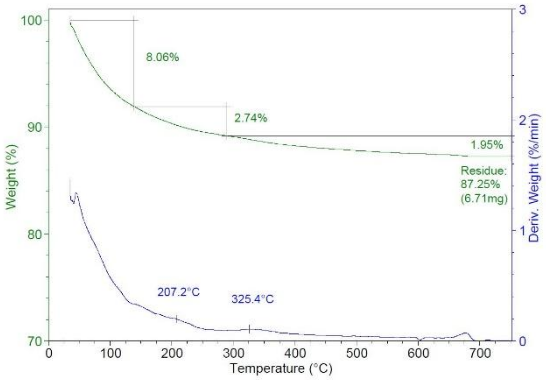
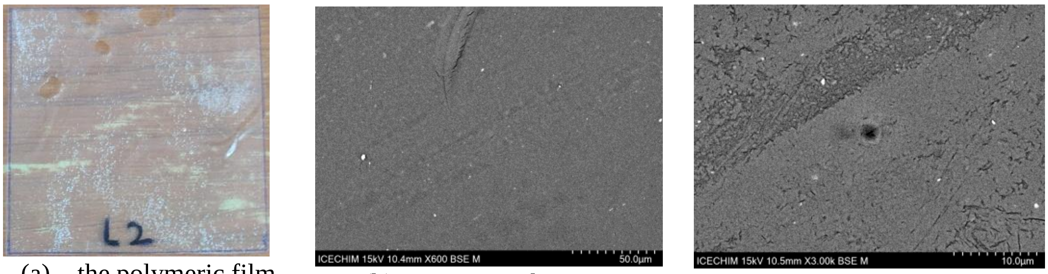


Fig. 7. Thermogram of hydroxyapatite substituted with Co.

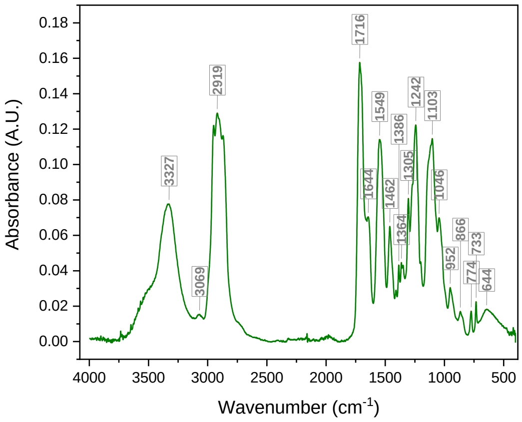
After it has been cast in silicon mould and cured, the polymeric film without filler was characterized using SEM. The images obtained are presented in fig. 8. In the Fig. 8 (a) it can be observed that the film is transparent, but it has microbubbles of CO_2 due to the reaction with condensed water vapour. The x600 micrograph, Fig. 8 (b) reveals a smooth surface, while the x3000 micrograph, Fig. 8 (c) depicts a microbubble along with minor surface defects.



(a) – the polymeric film (b) – micrograph, x600 (c) – micrograph, x3000

Fig. 8 - SEM micrographs of the polymeric film

The FTIR spectrum acquired for the binder-only film is shown in Fig. 9, while the correlations between the most relevant functional groups and the peaks are presented in table 2. It can be observed that the specific functional groups assigned to the IR bands [δ (N-H) - 1549 cm^{-1}; ν (C-O-C) - 1242 cm^{-1}; ν (N-H) – 3327 cm^{-1}, ν (C=O) – 1716 cm^{-1}] confirms the formation of poly(urethane) bonds**[32]**. It can also be observed that ν (C=C) – 3069 cm^{-1} is present because of the unsaturated fatty acids (mostly ricinoleic acid) present in the castor oil**[33]**.



Functional group	Wavenumber (cm^{-1})
δ (N-H)	1549
ν (C-O-C)	1242, 1103
ν (O-H)	3496 (should.)
ν (N-H)	3327 (broad)
ν_s (CH_2)	2919
ν (C=O)	1716
δ_{as} (CH_3)	1462
δ_s (C-H_3)	1386
δ (O-H)	1364
ν (C-N)	1305
ν (C=C)	3069

Fig. 9 (left) – FTIR spectrum of the polymeric film and Table. 2 (right) – FTIR bands - functional groups assignment

The differential thermogram of the polymer is presented in Fig. 10. In the first scan, a major endothermic peak can be observed, peaked at 67.99 °C, with an enthalpy of 34.89 J/g. This transition can be explained by the elimination of small molecule compounds (acetone, b.p. – 56 °C) or it can be assigned to the relaxation endothermic enthalpy, after the sample was aged below the glass transition temperature**[34]**. The glass transition temperature can be weakly correlated to the transition that peaks at 16.67 °C

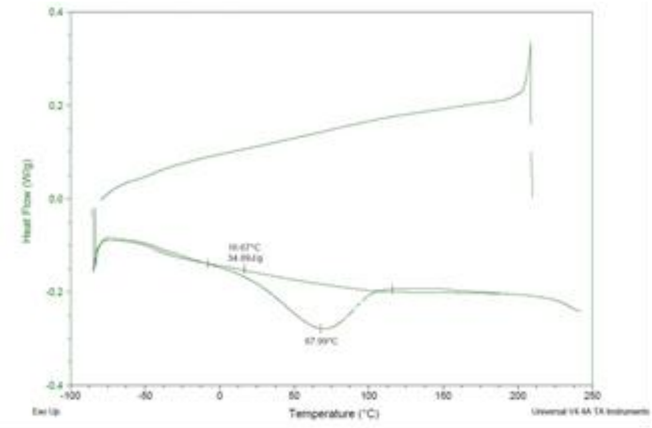


Fig. 10. The DSC thermogram of the polymeric film

To apply the compounds on aged wood, they were immersed on all sides in the polymer solution, then left to dry for 48 hours at room temperature. To observe the surface effects that the polymer solution had, the wood samples were morphologically characterized using the SEM technique.

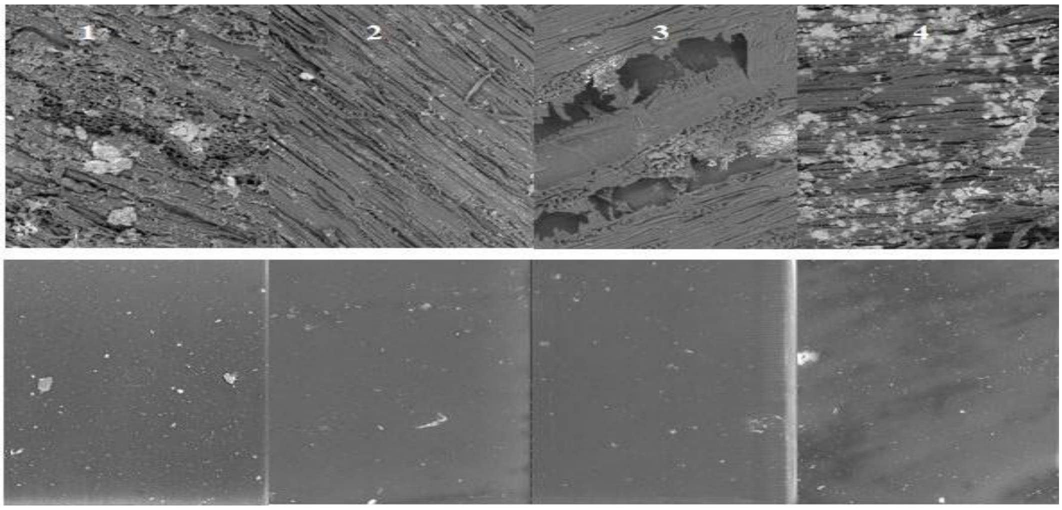


Fig 11 SEM images of untreated aged wood (up) and of treated aged wood (down) 1-fir, 2-ash, 3-pine, 4-oak

As it can be seen from the SEM images (Fig. 11), the aging treatment perfectly simulated the effects that the wood would suffer if it were stored for decades in the aquatic environment (Fig. 11 up). It can be seen how on the different types of wood, the water has left multiple cracks, fissures and ditches, causing irreparable damage. Moreover, thanks to the rigid structure, when they are taken out of the water, they will immediately suffer even greater and more aggressive damage caused by oxygen and biodeteriogens that will easily penetrate the structure of the wood mass. To solve this problem, we applied the synthetic materials on all four surfaces of the wood. As it can be seen from the SEM images (Fig. 11 down), the materials filled the cracks and fissures in the wooden mass caused by water, giving it a smooth appearance. The polymeric part of the composites is responsible for strengthening the wood structure, improving the mechanical properties and at the same time blocking the penetration of oxygen into the wood structure, while the apatitic component, having antimicrobial properties, will protect the wood against bacteria and fungi. The apatite materials showed antimicrobial activity on the tested bacteria (*B. subtilis* and *P. aeruginosa*) and fungi (*A. niger*).

Wood/Test	Treatment	Gloss (GU)	Color (ΔE)
Ash	M	0.43	-
	Co1	17.26	12.43
	Co2	24.5	16.27
	Co3	30.83	38.33
Fir	M	0.76	-
	Co1	19.56	17.19
	Co2	27.66	51.52
	Co3	19.46	11.35
Pine	M	0.5	-
	Co1	34.46	36.79
	Co2	31	11.49
	Co3	22.7	33.73
Oak	M	0.13	-
	Co1	29.46	30.37
	Co2	30.16	29.68
	Co3	27.63	32.61

Table 3 - **the results of the color and gloss tests for the cobalt-based treatment**

Wood/Test	Treatment	Gloss (GU)	Color (ΔE)
Ash	M	0.43	-
	Zn1	19.53	12.85
	Zn2	26.8	11
	Zn3	25.76	13.23
Fir	M	0.76	-
	Zn1	19.56	10.73
	Zn2	35.13	12.64
	Zn3	19.36	10.11
Pine	M	0.5	-
	Zn1	31.06	25.06
	Zn2	36.46	13.78
	Zn3	26.53	29.67
Oak	M	0.13	-
	Zn1	27.83	21.34
	Zn2	36.46	26.7
	Zn3	26.7	36.71

Table 4 - **the results of the color and gloss tests for the zinc-based treatment**

The values for the gloss and color tests are presented in table 3-4. The encodings in the table Co1, Co2, Co3 and Zn1, Zn2, Zn3 represent the amount of apatite material doped with heavy metals (cobalt and zinc), namely: polymer Co1 contains 0.166 g of apatite material doped with cobalt, Co2 contains 0.25 g of apatite material doped with cobalt and Co3 contains 0.5 g of apatite material doped with cobalt. The same principle is preserved in the case of Zn 1, Zn2, Zn3 polymers, the only change being that in this case the apatite material is doped with zinc, but the amounts of apatite material remain unchanged as in the case of polymers containing apatite material doped with cobalt. According to the literature, the aged blank shows a low gloss and by applying the treatment, these values increase, placing the samples in the category of objects with a low to medium gloss. The results of the color tests according to the literature are located in the area where there are small changes in shades (more intense) of the color. The treatment itself does not affect the color of the wood, as the recorded color change is caused by the aging process (Fig. 1). Although the aesthetic aspects are quite affected by the aging process, after applying the treatment, the wood acquires increased mechanical resistance and antimicrobial protection

4. Conclusions

One of the most well-known values that cultural heritage has in society is represented by its historical value, which is a continuous source of learning and knowledge. In addition to the historical value, it also has an economic and touristic value, many countries managing to develop economically by exploiting heritage objectives. Based on these aspects, several scientific fields have been developed, having as main goal the development of materials to preserve and conserve objects of cultural value. The present study demonstrated the development of a composite material consisting of two phases: an apatitic part that provides antimicrobial properties to the wood mass and a polymeric part with the role of filling the cracks and increasing the mechanical properties. The nanocomposite material was used as a consolidant material for samples that simulate waterlogged wood. After applying the polymers to the various wood samples, it was observed that the composite filled the holes and cracks caused by water, improving the mechanical properties of the samples. Moreover, the polymer works as a barrier between the wood and the external environment, protecting it from oxygen, bacteria and fungi.

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