Sustainable Materials and Technologies 30 (2021) e00348

Contents lists available at ScienceDirect

Sustainable Materials and Technologies

journal homepage: www.elsevier.com/locate/susmat

Mechanical properties and antimicrobial activity of pumice stone/sludge filled thermosetting composites

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ARTICLE INFO

Keywords:
Ecocomposite
Antimicrobial activity
Mineral waste
Pumice stone
Quarry sludge

ABSTRACT

The exploitation of natural quarries generates a high amount of waste as a result of the extraction, screening and segmentation processes. These usually inert wastes are not typically reused and end up in landfills. There is an urgent need for sustainable solutions aiming at the valorisation of these mineral wastes through the development of innovative products with greater added value and active functionalities. In this work, the applicability of different mineral wastes was tested on the development of advanced active ecocomposites. Several formulations/conditions, using green epoxy and polyester matrixes, were assessed in order to determine the reasonable production parameters. Additionally, two different antibacterial agents were added and the efficacy was tested. The overall mechanical performance of the ecocomposite was evaluated during every stage of development. The combination of dried sludge and green epoxy resin (SE_70), containing 70% of mineral waste, revealed to be most promising composition with interesting mechanical properties (tensile strength 91.63 ± 3.31 (MPa); strain (%) 0.69 ± 0.05; and Young's modulus (GPa) 13.65 ± 0.64). The functionalization of these samples was successful and the antibacterial activity was confirmed. However, the active agent affected the short-term mechanical properties. Nevertheless, the QUV® accelerated weathering test confirmed that the main long-term properties were unaffected. Thus, it is concluded that mineral waste from quarry activities can be use in the development of new sustainable added value advanced products.

1. Introduction

The mineral exploitation industries are essential for promoting industrialization and economic development in any region. However, the increasing amount of solid waste generated from the extraction and production processes is practically inevitable [1]. Additionally, parts of these solid residues are difficult to handle and occupy large areas of agricultural land, which causes a great impact on the environment [1,2]. This situation becomes even more complex when the terrestrial territory is limited and dispersed, as is the case of the Azores Archipelago (Portugal) [3]. Although it is responsible for an EEZ (exclusive economic zone) with about 954,496 km^2, its total land area is only 2333 km^2, distributed over 9 islands [4]. These islands are rather isolated, being far away from both Europe (1641 km) and North America (2985 km) continents [5]. The ultraperipheral and island condition, although it offers advantages at other levels (e.g., tourism), also entails logistical constraints such as the scarcity of raw materials, the need to import finished products and/or raw materials, and the increased transport and distribution costs [6].

More and more, there is an increase in the awareness of governments and other entities in general, about the environment and the sustainability of the resources available in nature. Therefore, it is very

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https://doi.org/10.1016/j.susmat.2021.e00348
Received 29 July 2021; Received in revised form 14 September 2021; Accepted 15 October 2021
Available online 20 October 2021

important to adopt new strategies to add value to local resources and unconventional materials in order to innovate and develop sustainable products. One possible strategy towards this end is exploring material substitution, such as polymeric matrixes, to enable lower-impact production and/or use.

In thespecific case of natural quarries, their exploitation generates a high amount of waste as a result of the extraction, screening and segmentation processes. These generally inert wastes are not typically reused for any added valued application, often ending up in landfills. Thereby, the need arises to find new solutions for the recovery of these mineral wastes that can truly enhance their characteristics and properties and, in this way, originate products with greater added value, valuing their aesthetic and functional components.

In the literature, it is possible to find several examples of studies for the recovery of mineral residues, including the extraction of metallic elements [7,8], and mineral components [9], the production of construction raw materials [10], power generation [11,12], building materials [13], and gas and water treatment [14,15].

However, due to the complexity and high costs of waste recycling and recovery processes, in practice, the amount of reused solid waste is low [1]. Thus, there is a need to improve and promote the recovery of waste, in particular mineral aggregates, in order to encourage global environmental management and sustainable development.

In this context, mineral waste has presented itself as a promising alternative as a reinforcement material for the development of new composites. In turn, the use of polymeric matrices is increasingly frequent, replacing conventional materials such as steel, aluminium, among others [16]. This trend is largely justified by the exceptional characteristics of this type of material, namely regarding its lower density and cost, in addition to minimizing the possibility of corrosion of these materials over time [17,18]. Allied to these factors, polymers are equally versatile and durable, besides the fact that there is no damage in terms of their mechanical properties in the final products, compared to traditional materials [18,19]. On the other hand, and in line with the development of material science and engineering, these advantages can also be increased by combining polymers with mineral fillers, as in the case of sand extraction residues, resulting in composite materials [2].

The present work intended to evaluate the applicability of different mineral wastes, from a local Azorean natural sand production quarry, on the development of ecocomposites. The effects of different factors such as the particle size, moisture content, composite and type of polymeric matrices, on the engineering properties of mineral waste slag ecocomposite were analysed in order to determine the reasonable production parameters. Finally, for the best composition, two different antibacterial agents were added and the efficacy was tested as well as the durability.

2. Materials and methods

2.1. Materials

Reagents: Ethyl alcohol 96% pure p.a. supplied by Merck (Madrid, Spain) and distilled water. The matrix-polymers: Epoxy - SR GreenPoxy 56, in which about 56% of its molecular structure comes from plants, giving this polymer an “eco-friendly” character ($\rho = 1.198$ gcm-3 and a $\eta = 800$ mPas, at 25 °C) provided by Sicomin (Châteauneuf-les-Martigues, France). Polyester - Resipur 9043 (orthophtalic unsaturated polyester resin of medium reactivity), ($\rho = 1.12$ gcm-3, $\eta =$ of 300 mPa s, at 25 °C, provided by Omnova Solutions, (Sintra, Portugal). Antimicrobial additives: ST1085, provided by SteriTouch and Argiblock, provided by Laboratorios-argenol (Zaragoza,Spain).

Antimicrobial activity assays: Microorganism used to test the antimicrobial activity was *E. coli* ATCC 10536. Trypticase Soy Agar (TSA), Triptone Salt Broth (TSB), Eugon LT broth were all provided by Biokar (Pantin Cedex, France). Assays were performed according to ISO 22196: 2011 [20].

2.2. Preparation of ecocomposites

First, the minerals were dried to remove excess water, for 12 h, at 50 °C, and then sieved by particle size, using molecular sieves size of 250 μm, to obtain an average particle size of 500 μm. Exception made to one set of samples produced with sludge, which was used as collected (SE_70_0h). The different minerals were the following: pumice stone, sludge (designation given to a mixture of various types of minerals resulting from quarrying) and a prepared mixture (formulation containing pumice stone and dry sludge 4:1 (*w*/w)). Table 1 shows the different formulations analysed during this work.

The combination of the elements (polymeric matrixes, hardener and mineral reinforcement) was carried out in a recipient followed by mechanical stirring, at room temperature (22 ±2 °C), respecting the manufacture indications regarding the ratio matrix:hardener. The samples were prepared following adapted protocols described in previous work [21].Briefly, the mixtures were transferred to moulds in which releasing agents were applied for easy removal of the composite. Samples were submitted to compression moulding cycle pressure – heating to 80 °C, applied pressure of 30 bar for 10 min followed by cooling to 50 °C under pressure) in order to eliminate the entrapped air. Following the curing process, the samples were cooled at room temperature and then demoulded.

2.3. Preparation of antibacterial eco-composites

The study of the effect of incorporating different antibacterial agents was conducted only regarding the optimal mineral reinforcement load, which was set at 70 vol%. Additionally, in order to maximize the sustainability of the final product, the work proceeded using only the eco-friendly matrix (GreenPoxy).

The preparation of the antibacterial eco-composites followed the same protocol mentioned above. The antibacterial agents were added during the mixing stage, following the indications of the manufacturer. Table 2 shows the composition of the different formulations with antibacterial agents incorporated.

2.4. Characterization of the prepared eco-composite

2.4.1. Mechanical properties

Mechanical characterization in quasi-static 3 point bending test was carried out in accordance to EN ISO 178 (04/2006) [22]. The testing was conducted with a Shimadzu-AG-IS, using a load cell with a capacity of 2.5 kN. The crosshead displacement rate was set at 2.0 mm min^{-1} and the specimens used were bars of a rectangular cross section (flatwise) with dimensions of 100x10x5 mm. The span length to sample’s thickness ratio was maintained at 16:1. All measurements were carried out at

Table 1
Different formulations analysed during the first part of the study.

ID	Mineral	Resin	% Mineral	Drying time
PPE_50	Pumice Stone	Epoxy	50%	12 h
PPE_70	Pumice Stone	Epoxy	70%	12 h
PPP_50	Pumice Stone	Polyester	50%	12 h
PPP_70	Pumice Stone	Polyester	70%	12 h
SE_70_0h	Sludge	Epoxy	70%	0 h
SE_50	Sludge	Epoxy	50%	12 h
SE_70	Sludge	Epoxy	70%	12 h
SP_50	Sludge	Polyester	50%	12 h
SP_70	Sludge	Polyester	70%	12 h
MixE_50	Mixture	Epoxy	50%	12 h
MixE_70	Mixture	Epoxy	70%	12 h
MixP_50	Mixture	Polyester	50%	12 h
MixP_70	Mixture	Polyester	70%	12 h

*Sludge: designation given to a mixture of various types of minerals resulting from quarrying.
**Mixture: formulation containing Pumice Stone and 4:1 dry sludge.

Table 2
Formulations with different antibacterial agents incorporated analysed during the second phase.

ID	Antimicrobial agent	% Antimicrobial agent incorporated
T1_SE_70	ST	0.5%
T2_SE_70	ST	1.0%
T3_SE_70	ST	1.5%
A1_SE_70	AB	0.5%
A2_SE_70	AB	1.0%
A3_SE_70	AB	1.5%
REF_SE_70	NA	NA

least 6 times, in a controlled environment at 21 ± 1 °C, with a relative humidity of 46%. All measurements were performed at least six times and the results are presented as mean values +/− standard deviation ($N \geq 6$).

2.4.2. Electronic scanning microscopy – SEM

In order to investigate the morphological aspects of specimen's, surface observations were made using a scanning electron microscopy NOVA 200 Nano SEM equipment from FEI Company. Before observation, the surfaces were vacuum coated with a thin layer of gold to make them electrically conductive.

2.4.3. Composite density determination

Density determination was performed according to the ISO 1183 [23] standard, using the immersion method, method A. Briefly, this method allows the determination of the density of solid substances, the same being defined as the quantity of mass occupied by a given volume. The prepared samples (10 × 10 mm) were dried for 24 h at 80 °C and the initial mass recorded (m_i). Next, they are immersed in the recipient containing the immersion liquid, ethanol and the final mass recorded (m_f).

Density was calculated as follows:

$$\rho = \frac{(m_i \times \rho_L)}{(m_i - m_f)} \quad (1)$$

where ρ_L is the density of the immersion liquid, in this case ethanol, (g cm^{-3}). Given that the measurements were performed at room temperature (22 ± 2 °C), the registered mass values were corrected to compensate for the effect of air buoyancy on the samples. In this sense, the value of the initial mass, (m_i), in Eq. (1), was corrected according to Eq. (2), where $m_{i,v}$ is the initial uncorrected mass, ρ_{air} is the air density and ρ_w is the density of the support weights used for the test pieces.

$$m_{i,v} = m_i \times \left(1 + \frac{\rho_{air}}{\rho} - \frac{\rho_{air}}{\rho_w}\right) \quad (2)$$

All measurements were performed at least in triplicate. The results are presented as mean values +/− standard deviation ($N \geq 3$).

2.4.4. Water absorption

Water absorption test was carried out to determine the amount of water to be absorbed by the samples. The assays were conducted in accordance to ASTM standard D570 and therefore, samples were prepared as per the standard dimension. First, the specimens were dried in the oven to remove the moisture content (24 h at 50 ± 1 °C). Next, the samples were weighed (m_i) and then immersed in distilled water for predetermined time (24 h and 48 h), after which the material was taken out, cleaned properly and weighed once more (m_f). The Water Absorption (%WA) was calculated as follows:

$$\%WA = \frac{m_f - m_i}{m_i} \times 100 \quad (3)$$

All measurements were performed at least in triplicate. The results are presented as mean values +/− standard deviation ($N \geq 3$).

2.4.5. Fourier-transform infrared spectroscopy – attenuated Total reflection – FTIR-ATR

FTIR spectroscopy was performed to characterize the chemical structure of the composites and to analyse the possible occurrence of chemical alterations induced by the antimicrobial additives. A Shimadzu IRAffinity-1S spectrophotometer was used to record the scanning spectra in the wavenumber interval between 4000 and 400 cm^{-1}.

2.4.6. Antimicrobial activity

Antimicrobial evaluation was performed according to ISO 22196 [20]. Briefly test materials were inoculated with microorganism *E. coli* ATCC 10536 (in a final concentration of 10^5 ufc/ml), incubated for 24 h at a temperature of 35 ± 1 °C and a relative humidity of not less than 90%. The reduction (as percentage) on the bacteria number was determined, and the antimicrobial activity (R) was evaluated according to the criteria established in ISO 22196, in which R is equal to the number of microorganisms counted on the untreated samples minus the number counted on the treated samples. All tests were done in triplicate, and nontreated samples were used as control.

2.4.7. Durability – accelerated weathering tester (QUV®)

The prepared samples were subjected to artificially weathering conditions using a QUV® chamber. This equipment applies a cyclic exposure with controlled irradiance, temperature, and humidity condition. All performed tests followed the protocol described in ASTM G 154 - *Standard Practice for Operating Fluorescent Ultraviolet (UV)*. Briefly, *an* UVA-340 lamps (irradiation of 0.71 W/m2 for 4 h) were applied to the surface of the samples for a total duration of 900 h, aiming to simulate the time of use in outdoor applications for 187 days. Each cycle was constituted, alternately, by two types of different stages, namely:

1) UV incidence stage: 8 h at 60 °C, irradiance (intensity of UV lamps) = 0.76; UV lamp wavelength = 340 nm (UV A).
2) Condensation step: 4 h at 50 °C.

In order to understand the evolution of this durability test, the samples were periodically removed from the QUV® equipment to assess the colour changing properties. To minimize the effect of the presence of moisture in the samples, measurement occurred only during UV cycle. The colour was evaluated using a spectrophotometer SF600 + C.T., series 4660 and the measurement diameter was 30 mm in order to minimize any effects caused by possible surface heterogeneity.

3. Results and discussion

3.1. Optimal formulations and mechanical properties

In this work, two different polymeric matrixes were evaluated. On one hand, epoxy resins were chosen due to their known ability to bond well to mineral fibres such as glass fibres [24]. Also, there matrixes are very interesting since greener solutions, such as green epoxy is also available, which has up to 56% of its molecular structure originating from plants [25]. On the other hand, polyesters are a widely used class of polymer due to their excellent processing, mechanical and recycling properties [26].

Both Epoxy and Polyester resins are thermosetting materials, generally, used for the manufacture of elements having to undergo high mechanical and thermal stresses. Epoxy resins are characterized by good mechanical and thermal resistance superior to those of polyesters, implementation possible without solvent, good resistance to chemical agents, very low uptake of humidity in immersion and excellent adhesion to fibres and metals [27].

Polyester is a high-performance thermosetting polymer and a low cost, is widely employed as packaging materials, owing to hardness, abrasion resistance, solvent resistance, electric insulation and good rigidity [28].

The main goal was to infer upon the optimal composite formulation by analysing several factors, such as: the type of mineral waste that led to better properties, the maximum % of mineral waste that could be incorporated without detrimental effects to the main properties. In this sense, various types of minerals, resulting from quarrying activities, were studied in combination with the two well-known polymeric matrixes.

Table 3 shows the results regarding the mechanical properties. The substantial effect of the pre-drying time observed (comparing samples SE_70_0h with SE_70 (Fig. 1 A and C) was expected since, generally, the presence of water affects the curing process of resins [29]. Studies have shown that water occupies the free volume of uncured resin, but after curing, the density increases, and as a result the water is no longer able to fit in the free volume and creates nanophase separation (visible in Fig. 1 by the difference of colour between samples A and B). Nanophase separation tends to prevent curing and decrease glass transition temperature [29]. This can be observed in by comparing the difference in colour between (A -SE_50_0h and B SE_50).

Additionally, this can also explain the considerable increase of mechanical properties (~85%), from 13.02 ± 0.74 MPa for SE_70_0h (no pre-drying time) to 91.63 ± 3.31 for SE_70 (subjected to a 12 h pre-drying time) (Table 3).

For the epoxy samples, it is clear that the increase of mineral filler (from 50 to 70%) led to an increase in tensile strength for all samples: from 37.81 ± 1.24 to 90.96 ± 5.69, in the case of pumice stone fillers, from 72.49 ± 1.58 to 91.63 ± 3.31, in the case of dried sludge fillers and from 44.69 ± 0.83 to 56.25 ± 1.38, in the case of the mixture fillers. This suggests that, at these proportions, the mineral is acting as a reinforcement rather than a filler. The obtained results are supported by literature, for example, Matykiewicz et al. [30] found that the thermo-mechanical properties of the epoxy composites improved with increased contents of basalt powder mineral filler. It is important to specify the meaning of each role: a reinforcement constitutes the reinforcement or the skeleton which provides the mechanical strength (tensile strength and rigidity), while a filler is refer to as any inert substance which, added to the base polymer, makes it possible to appreciably modify the mechanical, electrical or thermal properties, to improve the surface appearance or to simply reduce the price of the transformed material [27].

In the case of the polyester-based composites, there was no significant effect with the increase of mineral incorporation (Table 3). In fact, in some cases, a slight tendency for the mechanical properties to decrease was observed, for example, in the case of pumice stone, for which the tensile strength went from 35.93 ± 2.56 MPa to 31.26 ± 0.64 MPa. These results suggest that, at these %, in the case of polyester resin, the minerals are acting more as fillers rather than as reinforcement agents.

Based on these findings, it was possible to select the optimal formulation. The results show that, for green epoxy composites, 70% of mineral led to better mechanical properties, which is very interesting from the sustainability point of view. Furthermore, the sludge mineral was considered to be of higher interest. Out of all the studied minerals, the sludge represents one of the highest volume of waste generated during quarrying (25%). Moreover, when compared to the other minerals, specifically pumice stone, sludges are the residual waste with no economic value or secondary use other than landfill. Thus, from both the sustainable and economical points of view, an ecocomposite made of 50–70% (*W*/W) of a residual mineral waste with no other application, is very interesting. In this sense, the study proceeded to characterize and functionalize the best performing and eco-friendly solution: sludge: green epoxy ecocomposite.

Table 3
Results of the mechanical testing.

ID	Tensile strength (MPa)	Strain (%)	Young modulus (GPa)
PPE_50	37.81 ± 1.24	3.35 ± 0.34	2.78 ± 0.33
PPE_70	90.96 ± 5.69	1.01 ± 0.02	9.37 ± 0.39
PPP_50	35.93 ± 2.56	0.48 ± 0.06	7.68 ± 0.50
PPP_70	31.26 ± 0.64	0.35 ± 0.01	9.70 ± 0.17
LE_70_0h	13.02 ± 0.74	0.58 ± 0.07	0.59 ± 0.08
LE_50	72.49 ± 1.58	0.90 ± 0.11	8.30 ± 0.85
LE_70	91.63 ± 3.31	0.69 ± 0.05	13.65 ± 0.64
LP_50	41.03 ± 2.27	1.84 ± 0.17	2.32 ± 0.16
LP_70	40.56 ± 0.90	0.43 ± 0.03	9.79 ± 0.70
ME_50	44.69 ± 0.83	0.82 ± 0.04	6.08 ± 0.21
ME_70	56.25 ± 1.38	0.48 ± 0.02	12.01 ± 0.21
MP_50	44.18 ± 2.45	0.55 ± 0.02	8.19 ± 0.42
MP_70	44.94 ± 0.92	0.24 ± 0.01	19.75 ± 0.34

$N \geq 6$.

3.2. Characterization and functionalization

Regarding the characterization of the optimized formulations, the density and water absorption results are shown in Table 4.

As mentioned before, during the production of the composites different voids may occur, caused by air or humidity presence, which can in turn affect the final properties of the cured samples. In this sense, a considerable increase in density as a result of pre-drying the minerals, was observed (SE_70_0h:1.50 $g.cm^{-3}$; SE_70:1.92 $g.cm^{-3}$) (Table 4) [29]. Also, the increase in mineral content from 50 to 70% showed a slight tendency to increase density. Although the results did not show statistical significance, this is an expected effect [31].

Regarding the water absorption, according to literature, epoxy matrix composites generally absorb moisture and that this absorption can alter behavior of certain properties [32]. The water absorption is reasonably well described by classical diffusion law [32]. The obtained results show that the increase in mineral content led to a decrease of water absorption. This is expected and in accordance with literature [33], being that silica-based fillers tend to provide superior water resistance. Additionally, the values of W_a (%) were found significantly low and were observed to be minimum for LE_70 (0.2%). This confirms the hydrophobic nature of present silica-based minerals and the fact that the water absorption is related to the hygroscopic behavior of the polymer.

In order to assess the viability of functionalizing the ecocomposites to incorporate antimicrobial activity, two different commercial additives where studied, at 0.5, 1 and 1.5%. The results from the antimicrobial activity assays are presented in Table 5.

It can be observed that with the exception of sample SE_70_T1 all samples showed antimicrobial activity, being higher in samples with additive A, in which a complete inactivation of bacteria was obtained. Similar results were obtained by Pittol et al., work in which styrene-ethylene/butylene-styrene based thermoplastic elastomers (TPE) were also incorporated with zinc pyrithione (ZnPT) at 1.5% [34] The incorporation of additives in the composites was successful, resulting in samples with antimicrobial activity.

Regarding the chemical structure of the active ecocomposite, the antimicrobial agent A's main active component is zinc pyrithione (2 mercaptopyridine N-oxide zinc salt) (Fig. 2), which, according to literature, presents several characteristic peaks in the FTIR spectra [35].

However, the FTIR-ATR analysis performed, shown in Fig. 3, indicates that no significant chemical alterations could be observed because of the incorporation of the active agent. This could be related to the small % that was used. Nevertheless, is was possible do observe the main characteristic peaks, as follows: from 2965 to 2873 cm^{-1} corresponded stretching C-H of CH_2 and CH aromatic and aliphatic [36,37]; 1608 corresponded to stretching C=C of aromatic rings [36]. Also, 1509 and 826 cm^{-1} related to the presence of benzene ring. Furthermore, the absence of unreacted epoxy was confirmed by the absence of the corresponding epoxide group peak at 910 cm^{-1}. This indicates that the curing process was complete and the amount of hardener used was adequate for the curing reaction to reach completion, irrespective of the filler amount [37].

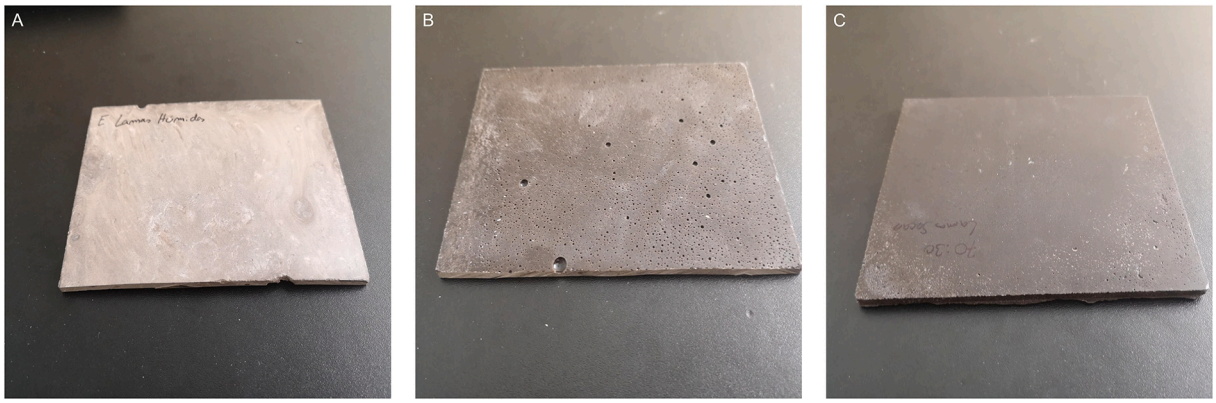

Fig. 1. Representative eco-composite samples. A - Sample produced with wet sludge (SE_50_0h); B - Sample produced with dry sludge (SE_50); C - Sample produced with dry sludge (SE_70).

Table 4
Density and water absorption results for optimized formulations.

ID	Density (20 °C) g.cm^{-3}	Water absorption (%)
GreenEpoxy[a]	1.198 ± 0.005	NA
LE_70_0h	1.50 ± 0.01	9.3 ± 0.8
LE_50	1.62 ± 0.01	3.5 ± 1.5
LE_70	1.92 ± 0.01	0.2 ± 0.0

[a] Technical data sheet information; $N = 3$.

Table 5
Results from the antimicrobial activity assays.

Sample ID	Additive ID	%	Antimicrobial activity – R (% of inactivated bacteria)
SE_70_T1	T	0.5	−1.13 (0)
SE_70_T2	T	1.0	0.82 (14.6)
SE_70_T3	T	1.5	4.68 (82.7)
SE_70_A1	A	0.5	3.27 (49.5)
SE_70_A2	A	1.0	5.97 (100)
SE_70_A3	A	1.5	5.25 (100)

$N = 3$.

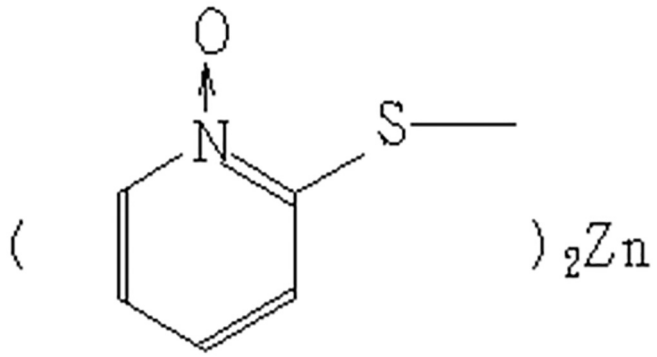

Fig. 2. Chemical formula of Zinc pyrithione, molecular formula: $C_{10}H_8N_2O_2S_2Zn$.

When analysing the SEM micrographs it is possible to observe an irregular characteristic aspect of the surfaces. This is reported by other studies regarding epoxy composites with high % mineral fillers [38]. Additionally, no noteworthy voids or other changes were observed for samples SE_70 as well for as samples containing the antimicrobial additives (Fig. 4). This indicates that the additive did not affect the surface morphology of the ecocomposite.

One of architectural elements' most important attributes is their ability to maintain performance for an extended period in their intended service environment. That environment may be an interior space in a single-family home or the exterior of a building. Moisture, rainfall, extreme temperatures, ultraviolet light, and pollutants cause the degradation of epoxy resin in the outdoor environment (mechanical performance).

In order to predict the long-term performance of the active eco-composite in a short amount of testing time, QUV® Accelerated Weathering Tests were performed. Accurate results require that the accelerated weathering conditions closely match the natural weathering conditions, but also enable an acceleration in the degradation rate compared to natural weathering. The mechanical properties of the studied active ecocomposites were measured before and after the QUV® test and are presented in Table 6.

The durability results show a significant decrease in the overall mechanical performance after the QUV® test. According to literature, hydrothermal ageing is one of the more frequent ageing conditions because of both temperature cycles and water absorption-desorption [39]. Moreover, water absorption is known to induce important transformation in the mechanical behavior of epoxies, including plasticization and degradation of the network structure, which may affect the strength and fracture toughness [39].

Additionally, QUV® cycles induce the formation of superficial degradation that alters the porosity. This leads to the formation of micro-bubbles, which then lead to micro-cracks, also contributing to the decrease of mechanical performance. This fact could be easily overcomed by projecting/designing the ecocomposite with a higher partial safety factor in order to secure the material's reliability, that is, assuring that the ecocomposite performs its purpose adequately for the period of time intended under the operating conditions encountered. Partial safety factors are used to take in to account the occurrence of unwanted deviations, inaccurate modelling or uncertainties in the assessment of the effects of actions, geometric properties and resistance model [40]. Therefore, the design considering higher partial safety factors could overcome the adverse effects of long-term use and guarantee the adequate performance [40,41].

Regarding the effect of the incorporation of the antimicrobial agent, it was observed that even at the lowest concentration (0.5%) the agent had a detrimental effect of the short-term mechanical properties. Sample SE_70_A1 revealed a decrease of 51% for tensile strength when compared to SE_70.

Although the chemical analysis did not show any structural alterations, it is possible that the antimicrobial agent can impair, in some way, the correct polymerization of the epoxy resin, thus resulting in the lower mechanical properties.

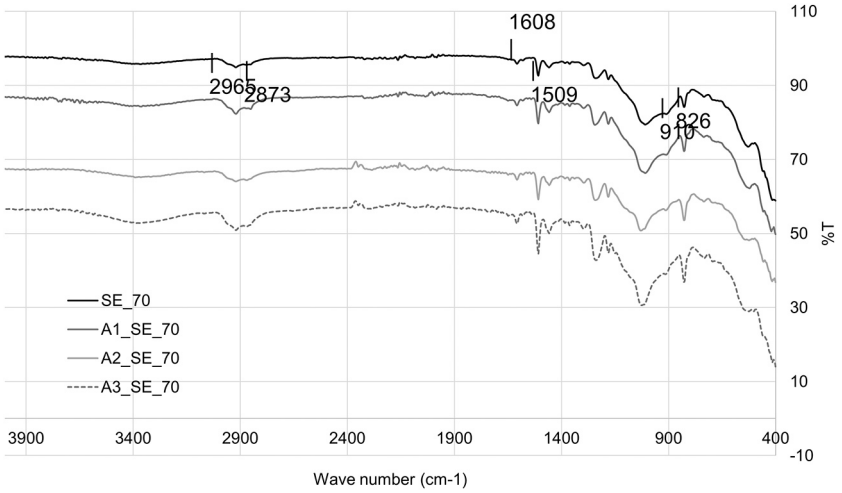

Fig. 3. FTIR-ATR spectral analysis (2965–2873: Stretching C-H of CH_2 and CH aromatic and aliphatic; 1509 Stretching C-C of aromatic rings; 910 Stretching C-O of oxirane group; 826 Stretching C-O-C of oxirane group).

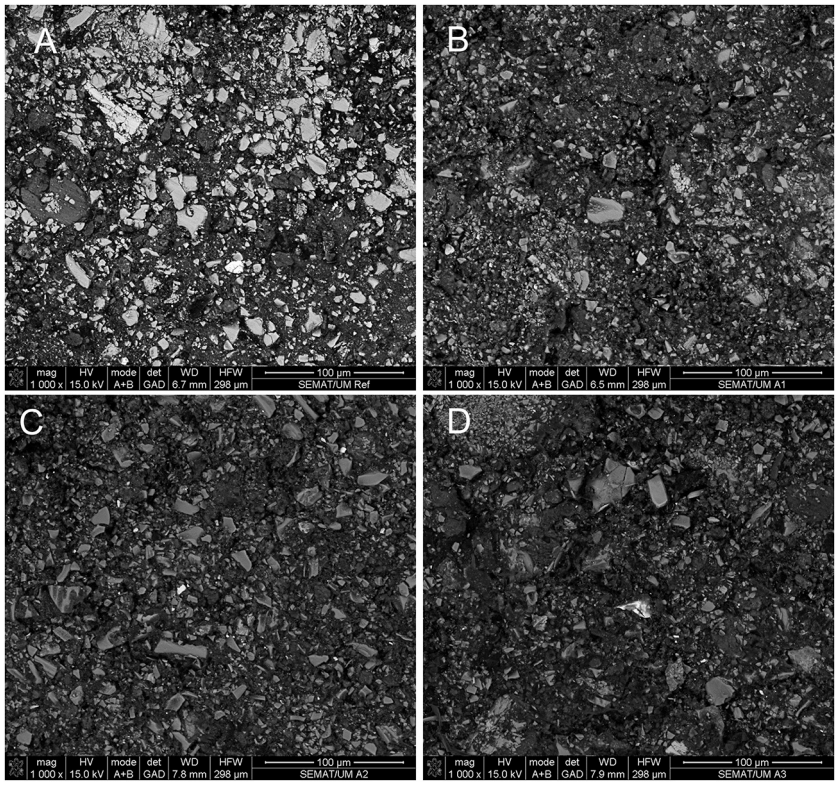

Fig. 4. Surface Morphology of: (A) SE_70; (B) SE_70_A1; (C) SE_70_A2; (D) SE_70_A3.

Table 6
Mechanical properties of the studied active ecomposites were measured before and after the QUV® test.

ID	Tensile strength (MPa)	Max strain (%)	Tension at break (MPa)	Strain at break (%)	Young modulus (GPa)
SE_70	91.63 ± 3.31	0.69 ± 0.05	91.63 ± 3.31	0.69 ± 0.05	13.65 ± 0.64
SE_70 ^{QUV}	50.64 ± 1.51	0.51 ± 0.02	50.54 ± 1.41	0.5 ± 0.0	10.41 ± 0.29
SE_70_A1	46.78 ± 3.69	0.57 ± 0.04	46.61 ± 3.80	0.57 ± 0.04	8.60 ± 0.72
SE_70_A1 ^{QUV}	50.47 ± 3.65	0.55 ± 0.03	49.92 ± 3.5	0.55 ± 0.03	10.90 ± 0.08
SE_70_A3	48.78 ± 4.92	0.50 ± 0.06	50.88 ± 4.95	0.50 ± 0.06	12.01 ± 1.01
SE_70_A3^{QUV}	40.58 ± 3.37	0.49 ± 0.03	40.20 ± 3.29	0.49 ± 0.03	9.40 ± 0.46

$N \geq 6$.

However, the obtained results show that the incorporation of the antimicrobial agent has little of no effect on the long-term mechanical properties of the developed composite. Maximum variations of ~10%, regarding tensile strength, were registered for the samples with the highest antimicrobial concentration (SE_70_A3 1.5%). Additionally, no considerable alterations were observed in terms of the values for young modulus.

4. Conclusion

This work shows that it is possible to develop active ecocomposites, using mineral wastes from quarry activities, in a sustainable manner.

An ecocomposite was developed using mineral wastes, from a local Azorean (Portugal) natural sand production quarry. Several formulations were studied, using thermosetting polymers as matrices, in order to defined the optimized and more sustainable solutions reasonable production parameters.

The combination of dried sludge and green epoxy resin (SE_70), containing 70% of mineral waste, revealed to be most promising composition with interesting mechanical properties (tensile strength 91.63 ± 3.31 (MPa); strain (%) 0.69 ± 0.05; and Young Modulus (GPa) 13.65 ± 0.64).

Additionally, it was possible to incorporate antibacterial additives successfully, resulting in samples with antimicrobial activity, whilst preserving chemical and morphologic features, as shown in the FTIR and SEM analysis. Furthermore, the accelerated weathering tests showed significant decrease in the overall mechanical performance after the QUV test for the samples without antimicrobial agent. This could be related to the formation of superficial degradation (porosity modification, formation of micro-bubbles and micro-cracks), thus resulting in the decrease of mechanical performance. Finally, regarding the effect of the incorporation of the antimicrobial agent, even at the lowest concentration (0.5%) the incorporation resulted in significant detrimental effects of the short-term mechanical properties (51% for tensile strength when compared to SE_70). Nevertheless, the incorporation of the antimicrobial agent has little of no effect on the long-term mechanical properties of the developed composite.

Declaration of Competing Interest

None.

Acknowledgements

This work was supported by Operational Programme “Regional Azores 2014–2020”, through project Basalt Waste Composite (ACORES-01-0247-FEDER-000013), Portugal.

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