Biomineralisation to improve properties of polymer modified concrete for chloride environments

Hazha Mohammed [a], Francesca Giuntini [b], Alan Simm [c], Monower Sadique [a], Andy Shaw [a], Ismini Nakouti [d], Ana Bras [a,*]

[a] Built Environment and Sustainable Technologies (BEST) Research Institute, Liverpool John Moores University, United Kingdom
[b] Pharmacy and Biomolecular Sciences, Liverpool John Moores University, United Kingdom
[c] Faculty of Sciences, Liverpool John Moores University, United Kingdom
[d] Centre for Natural Products Discovery (CNPD), School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, United Kingdom

ABSTRACT

This research compares the performance of three types of polymer-modified concrete (TPE, LDPE/EVA, and PCL) if bacteria-based solutions are used for reinforced concrete (RC) structures designed for a compressive strength higher than 50 MPa in chloride environments. The aim is to understand the impact on mechanical and durability performance of concrete. These recyclable polymers' use is crucial to increasing the strength at 28 and 60 days. At 60 days, all polymer-modified concrete reached a compressive strength higher than 60 MPa. The use of bioproducts is crucial to lowering the open porosity values to 4%. However, the use of bioproducts tends to delay the increase of concrete's compressive strength with time, especially until the 14 days. The existence of tetrahedron and pyramid structures in polymer-modified bio concrete indicates that calcite is present, and the quantity of calcium carbonate in the polymer-modified bio concrete is significantly higher than in plain bioconcrete or even plain. The bioproduct plays a dominant role in the capillary control and prevents water migration more effectively in comparison to the use of different polymers in concrete. The bioproduct substantially minimise the migration of chlorides to 7×10^{-12} m^2/s, a water-soluble ion in wet/humid concrete porous medium environments, but also at low relative humidity environments, as it happens when the concrete is exposed to capillary suction. The highest electrical resistivity values have been recorded in TPE bio-concrete.

1. Introduction

RC structures are highly affected by maritime environments, de-icing salts, moisture, and industrial chemicals, leading to structural deterioration. Polymer-modified concrete is primarily used in bridge decks, post-tensioned beams, and slabs; in pipes for the transport of fluids; in storage tanks for seawater; and in hazardous waste containment, among others. To strengthen the cement-hydrate binder, the polymers can be added to the concrete mixture as a partial replacement for sand. The objective of the polymer is to fill the voids in the concrete and prevent the free water movement usually found inside the voids of this porous medium [1]. By heating this type of concrete, reactive molecules will start the polymerization, spreading the polymer through the concrete voids and then convert it into a solid polymer.

Several factors affect the performance of concrete with polymer incorporated, and only a few types of polymers could be implemented in wet concrete repair. Concomitantly, the structure service temperature needs to be considered, as it can have a severe impact on the properties of the polymer-modified concrete [2]. The quick curing of polymer concrete may result in a shorter working time, which is important, especially when placing and finishing concrete, as it occurs on highway repair works where traffic disruption and time constraints are an issue.

It is estimated that the optimum amount of polymer to be added needs to be between 7.5% and 20% of the dry polymer solids/cement mass. Too much polymer might damage concrete, leading to air entrainment and promoting a mechanical behaviour of the concrete more similar to that of a polymer. A very low quantity of polymer in the concrete can slow down the development of the mechanical properties expected for the concrete [3].

There are mainly five different types of polymeric modifiers commonly used in concrete: water-soluble polymers, polymer dispersions, monomers, liquid resins, and re-dispersible polymer powders.

Table 1
OPC chemical analysis.

Element %	OPC
Fe_2O_3	2.62
CaO	68.91
SiO_2	19.99
MnO	0.06
Al_2O_3	4.32
MgO	1.21
TiO_2	0.18
Na_2O	0.22
K_2O	0.73
L.O.I.	4.00
Acid soluble Cl	0.07

These polymers tend to increase the workability of concrete and contribute to reducing the water/cement ratio [4,5].

The properties of concrete mixes containing various types of polymers have been investigated and reported [6–8]. Thermoplastics are the most frequently used in concrete to partially replace coarse or fine aggregates, including polyethylene terephthalate (PET), low and high-density polyethylene (LDPE and HDPE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS), etc.

The importance of polymer composites in the concrete industry is emphasised by the substantial number of topics related to polymers that can be found in the European standards, namely EN 1504. Their chemical resistance tends to be better than ordinary concrete, and polymer-based solutions can ensure a high level of adhesion, which is relevant in repair work to improve the adhesion of new to old concrete.

Cracks can cause corrosion of steel rebars by acting as a path in porous media in concrete for harmful particles dissolved in fluids and gases to compromise the durability of reinforced concrete. However, cracks can be minimised due to the rapid and high development of the tensile, compressive, and flexural strengths of polymer concrete in comparison to conventional concrete. Various types of polymers can be combined to be used in concrete to ensure the desirable "elasticity" of material solutions. This can enhance the fracture energy of concrete, increasing the elongation at rupture, e.g., from 2% to 10%, when compared to traditional concrete, or increase the tensile strength, minimising crack development [3,9]. Concomitantly, few works have reported the use of solid polymers in the study of reinforced concrete durability-related properties.

However, a major disadvantage of polymers is their high cost, the complicated and labour-intensive manufacturing process associated with their environmental impact [10,11]. Therefore, the challenge is to find a balance between:

The expected properties of reinforced concrete in terms of durability. The elasticity and crack control that polymers can offer in these structures.

The cost and environmental impact of industrially developed polymers.

Cost reduction could be obtained via recycling plastic waste, and this alternative can be feasible for producing new construction materials, such as cement composites. This is an economic and ecological solution and seems to be the best for disposing of plastic waste [8,12]. However, several important properties such as bond to bond strength, and durability of concrete and cement mortar are negatively affected if plastic is added [13,11]. Using biomineralisation techniques, it is possible to overcome these challenges [14,15].

Biomineralisation is the process by which living organisms (bacteria) form minerals as a result of their metabolic activities' interactions with the environment. Microorganisms cause precipitations of $CaCO_3$, which can stiffen or harden building materials, particularly those made of cement, and seal the cracks in the walls to lessen permeability [16–18].

This biotechnological healing method makes use of certain bacteria ability to induce calcium carbonate formation within the cementitious matrix. According to the working theory, these bacteria can generate calcium carbonate precipitations as well as biologically induced chemical precipitations, allowing the organism to develop a perfect mineral phase extracellular micro-environment known as biomineralisation. The metabolic route for the formation of calcium carbonate can sometimes affect the corrosion of cement-based materials [16,18–24]. The precipitation of $CaCO_3$ can happen in three different polymorphic forms: calcite, aragonite, and vaterite. $CaCO_3$ also occurs in an amorphous phase, which is a metastable phase of $CaCO_3$. Calcium carbonate precipitation is induced through different bacterial mechanisms, namely: sulphur cycle, iron respiring and nitrogen cycle which is divided to urea hydrolysis, amino acid ammonification and dissimilatory nitrate reduction [25]. However, the process needs to be compatible with the concrete matrix and should be economically viable.

After directly adding a specific type of alkalophilic bacillus to concrete, Jonkers et al. [26] looked at the bacteria's capacity to survive. According to the results, the rate of bacterial spore survival decreased by more than 90% in just one month. The author discovered that carrier technology might be used to increase the microorganisms' ability to survive. However, Mohammed et al. [17] observed that this strategy is a promising one for enhancing RC performance, particularly in the case of concrete mixed with plastic particles. This is because bacteria are added to fresh concrete during the casting process.

Furthermore, another method is to externally apply bacteria to the crack surface [27,28] or use microcapsules inside the concrete and activate them when the damage occurs [29,30]. Manual repair is required for pre-existing cracks. However, in the case of the need for intrinsic healing, the system needs to be installed at the time of construction, inside the concrete. An option could be the use of capsules for intrinsic healing, where they are spread in the concrete. Polymers such as polyurethane [31–33] and hydrogel [34] have also been used in the encapsulation method here. It has also been stated that the healing fluid is administered to the place of damage via capillaries or hollow channels in the vascular system [35,36].

However, due to a lack of systematic characterisation of properties in RC structures, the applications of these bacteria-based solutions to promote biomineralisation are currently limited [37–41].

As the $CaCO_3$ formed by bacteria in the cracks is a brittle material and mainly useful for healing of static cracks, the use of thermoplastic polymers will protect the bacteria in/ around the cracks and the combination can show a larger degree of elasticity that might allow to keep even a dynamic crack sealed. The use of bacteria-based solutions to complement the polymer-modified concrete might be an opportunity by potentially enabling the re-use or increase the quantity of polymers incorporated and simultaneously taking advantage of polymers' elastic/ ductile properties to heal concrete cracks in a complementary way to the calcium carbonate formed due to bacteria metabolism. This study aims to compare the performance of polymer-modified concrete for RC structures when bacteria-based solutions (bioproducts) are mixed in, as well as to understand the impact on the final physical and mechanical performance of concrete.

2. Materials and methods

2.1. Ordinary Portland cement

Ordinary Portland Cement (OPC) type CEMI 52.5N was used in accordance with BE EN 197-1: 2011. The OPC was supplied by Hanson Cement in the UK. X-ray fluorescence (XRF) was used to analyse the chemical composition of OPC, as shown in Table 1.

2.2. Aggregates

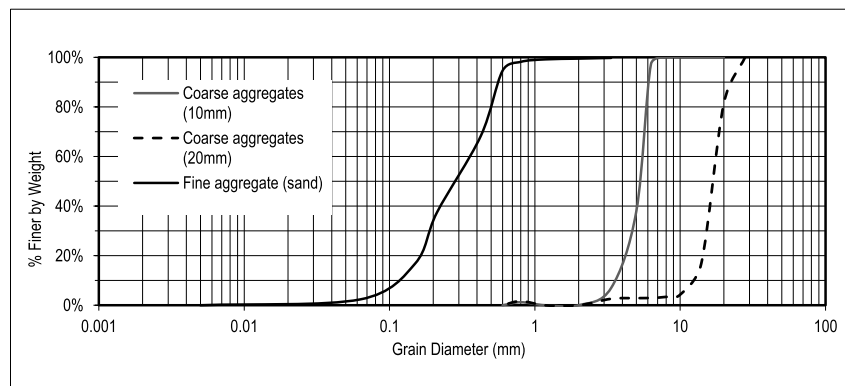The sand used in this study comes from Tarmac Plant, UK, according

Fig. 1. Particle size distribution for coarse and fine aggregates.

Table 2
Properties of the polymers used in the concrete.

Polymer type	Density (g/cm3)	Size (mm)
TPE (powder)	0.88	≥ 1.18
PCL (granular)	1.15	2
LDPE/EVA (powder)	0.9	≥ 1.18

to BS EN ISO 9001. Coarse aggregates were supplied by Specialist Aggregate and Travis Perkins in the UK; the aggregate sizes were 10 and 20 mm. Fig. 1 presents the particle size distribution for coarse and fine aggregates.

2.3. Polymers

A total of three types of thermoplastic polymers were selected for this study, as they are potentially recyclable, abundant in the built environment (e.g., plastic bags, bottles, storage containers, utensils) and have not been considered before in the durability of infrastructures [42]. The candidate thermoplastic polymers were used as fine aggregate replacement (3%) and as a bioproduct (bacteria) carrier in concrete. The polymers investigated include thermoplastic elastomers (TPE), low density polyethylene/ethylene vinyl acetate copolymer (LDPE/EVA), and -polycaprolactone (PCL).

TPE (SEEPS) is a block copolymer of styrene-[ethylene-(ethylene-propylene)]-styrene (TPS). They have both semi-crystalline or glassy blocks and amorphous blocks along the backbone. The amorphous blocks provide the elastomeric bridges between the crystalline domains. The benefit of TPE is its ability to stretch to moderate elongations and return to its near original shape, contributing to the increase in the structure's lifetime.

LDPE/EVA are made by the co-polymerisation of ethylene monomers, ethylene, and vinyl acetate to provide amorphous and elastic properties to the concrete. The polyethylene segments, which are crystalline in nature, are bonded together with the vinyl acetate group, the latter disrupting the crystalline nature of the system. Hence, the higher the vinyl acetate, the lower the crystalline nature of the concrete.

Due to its low cost, ease of manufacture, long durability, and chemical resistance to most unfavourable situations, LDPE has been widely used in industrial sectors [43]. LDPE/EVA are resistant to chemicals such as: calcium hydroxide, calcium oxide, carbon dioxide, calcium chloride, ferrous chloride, etc.

PCL, or Polymorph, is a linear polyester derived from caprolactone monomer that exhibits excellent chemical and solvent resistance and is a semi-crystalline, hydrophobic, biodegradable linear polyester. Due to its high molecular weight, PCL has mechanical properties and an oxygen permeability comparable to polyethylene (PE). Table 2 presents the TPE, LDPE, and PCL characteristics used in this work.

The x-ray diffraction (XRD) was analysed for the powder plastics (TPE and LDPE). The surface texture was analysed through SEM but presented in more detail later. Fig. 2 depicts XRD result for TPE. The partial crystallinity of LDPE/EVA was confirmed by an X-ray diffractogram, and the surface texture analysed by SEM is shown in Fig. 3, where peaks at 21.2 and 22.6 have been identified as characteristic.

2.4. Microbial agent and culturing

A strain from *Shewanella* genius was used as a bioproduct in this research, it was originally supplied by a German company. They are typically rod-shaped, 2–3 μm in length, and 0.4–0.7 μm in diameter. *Shewanella* is iron-respiring bacteria, uses oxygen as terminal electron acceptor during aerobic respiration; however, during anaerobic conditions, as it undertakes respiration by reducing other terminal electron acceptors such as oxidized metals, including ferric ion Fe (III), manganese oxide Mn (III), manganese dioxide Mn (IV), uranyl ion U (VI), hexavalent chromium Cr (VI), but also nitrate NO_3^- [44]. This ability to couple metal reduction activity with their metabolism puts *Shewanella* into a class of bacteria known as "Dissimilatory Metal Reducing
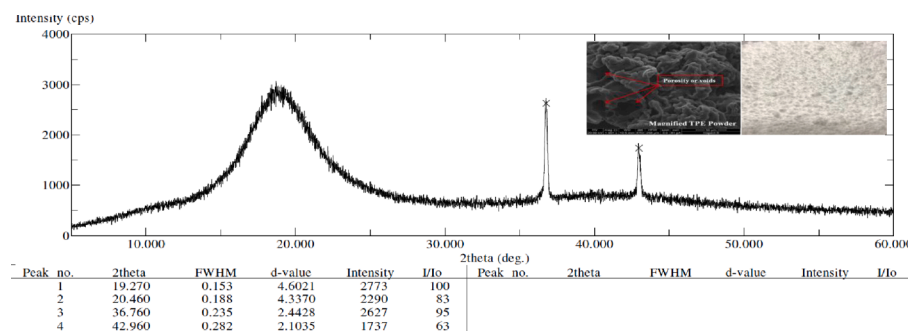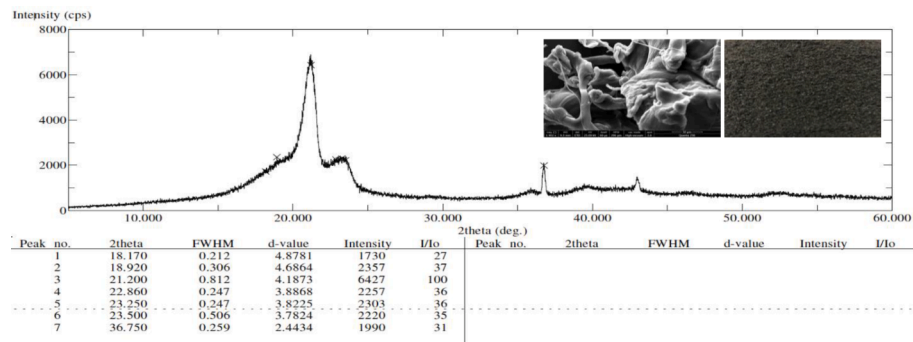

Fig. 2. X-ray diffraction of TPE.

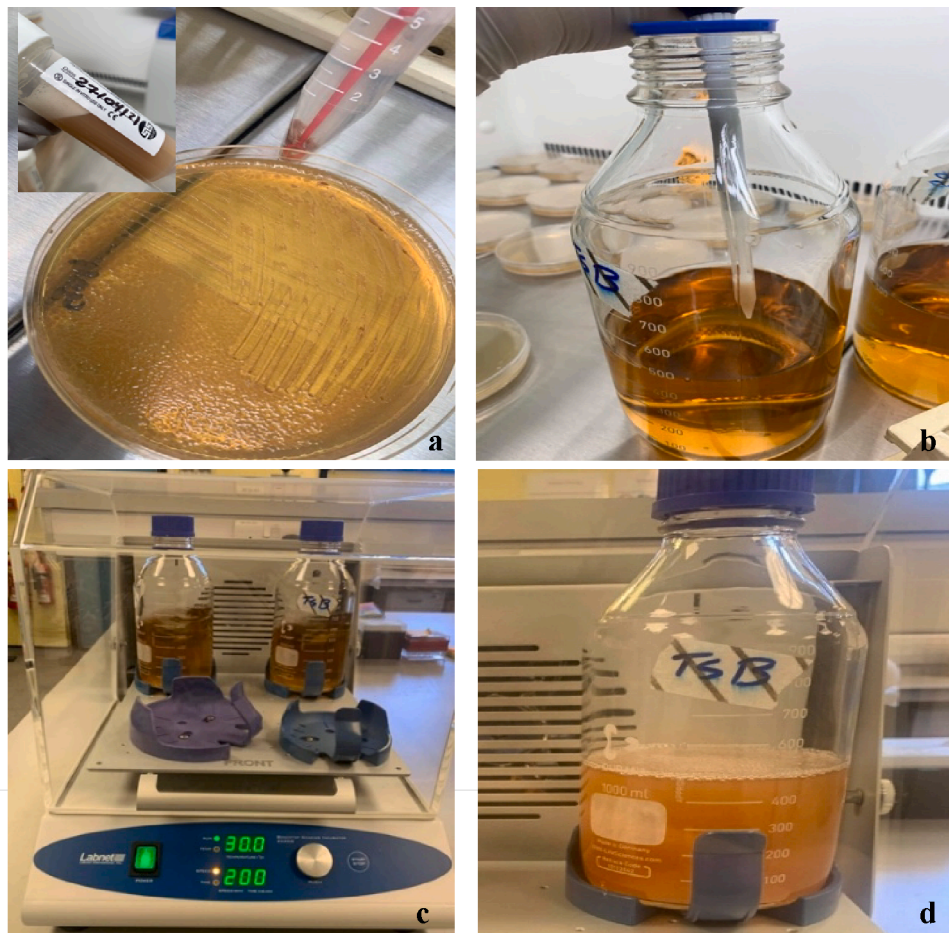**Fig. 3.** X-ray diffraction of LDPE/EVA.

Fig. 4. Sub-culturing and cultivating of *Shewanella*; (a) preparing concentrated *Shewanella* inoculum, (b) the concentrated inoculum added bacterial nutritional medium TSB, (c) the culture is placed in the benchtop shaking incubator at temperature 30 °C and speed 200 rpm, (d) bacterial culture after shaking.

Bacteria. A ratio of 2.1%/binder (Fig. 4) was added to a concrete batch. This iron-respiring bacteria has the ability to grow over a wide pH range 5.6 ~ 9.4 and at temperatures between 34 and 35 °C, where it grows fastest.

The bioproduct formation requires amino acids and other complex nitrogenous compounds through bacteria enzymatic digestion of casein and soybean. Dibasic potassium phosphate acts as a buffer to control pH. Sodium chloride maintains osmotic equilibrium. Therefore, Tryptic Soy Broth (TSB) is used as a nutritional medium to promote the cultivation of the microorganism.

2.5. Soaking the polymers in the bioproduct for concrete preparation

For the three types of polymers, soaking the polymer in the bioproduct was promoted to adhere it to the polymer surface or to impregnate the polymers with the bioproduct. Following that, the bioproduct and polymer combination was placed in a bench-top shaking incubator for 30 min at 30 °C and 200 rpm per minute (Fig. 5(a-c)), then mixed with fresh concrete (Fig. 5(d-f)). SEM imaging was performed on some samples.

2.6. Concrete mix design and preparation
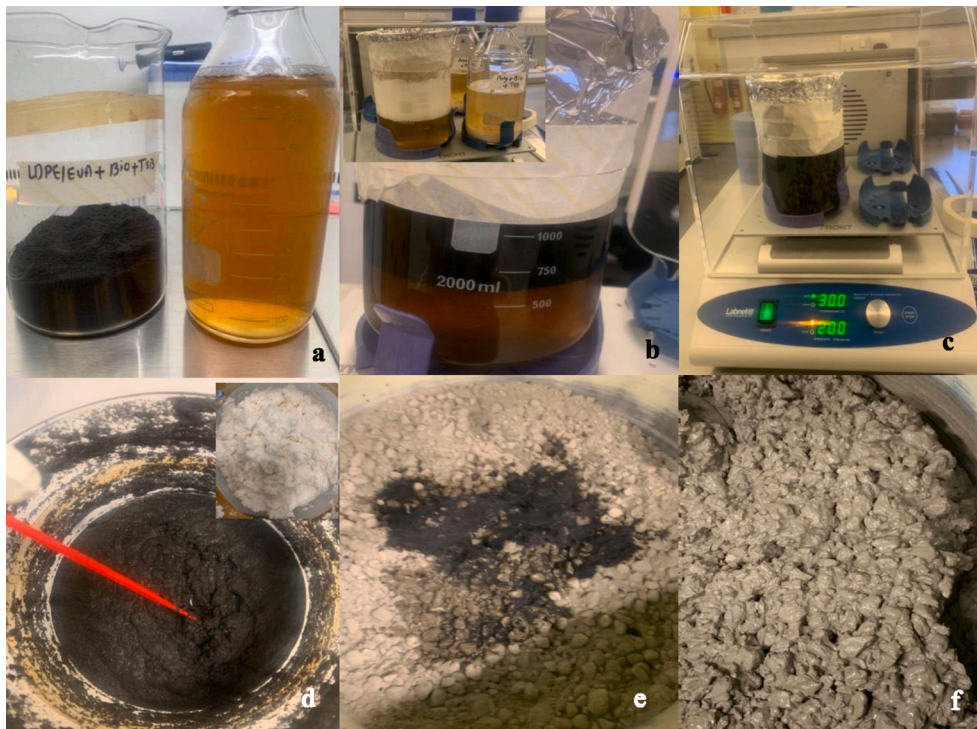
The polymers TPE, LDPE/EVA, and PCL were used as 3% sand

Fig. 5. Soaking polymers in the bioproduct and mixing it with fresh concrete.

Table 3
Concrete mix design.

Concrete Composition	kg/m³	Quantities (kg)
CEMI 52.5N	450	9.54
Aggregate 20 mm	712	15.1
Aggregate 10 mm	610	12.9
Sand	335	7.1
Water	180	3.8
w/c	0.4	
Polymers	10.05	3%
Bioproduct	–	50 ml

replacements (by weight of sand) in concrete. Eight concrete compositions were cast in accordance with BS 1881-113: 2011 [45]. The mixes were as follows: plain (control without polymer or bioproduct), plain + Bio (control with bioproduct), 3% TPE, TPE + Bio, 3% PCL, PCL + Bio, 3% LDPE/EVA, and LDPE/EVA + Bio. For each polymer-modified concrete, with and without bioproduct, 15 cubes of size $100 \times 100 \times 100$ mm and 5 cylinders with a diameter of 100 mm and a height of 200 mm

prepared and cast with water to cement ratio (w/c) 0.40 per concrete composition. After casting, the concrete samples were preserved under laboratory conditions for 24 h before demoulding, then cured in a water tank at 40 °C for 7 days before being moved to room temperature (20 °C) tank water for the remainder of the testing days. For porosity and capillary tests, all samples were dried in an oven at 35 °C until the mass change was less than 0.1%. Table 3 and Fig. 6 show the concrete mix design and preparation.

2.7. Laboratory experiments

2.7.1. Water loss analysis of the polymers

The water loss analysis of polymers was undertaken in order to investigate the absorption capacity of different types of polymers. Initially 5 g of each polymer with 20 ml of water were placed in a lidded petri dish and kept at atmospheric temperature for 2 h (with closed lids). The petri dishes were placed in an oven at 40 °C for 96 h, then the polymers were weighed to analyse how much water evaporated from the polymer.
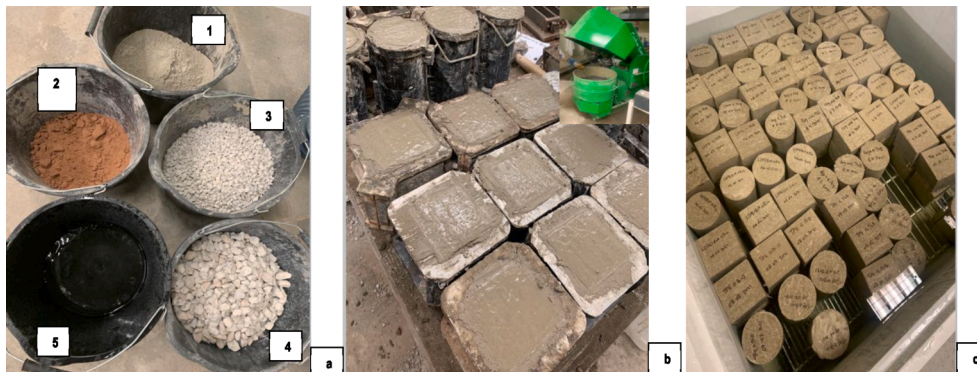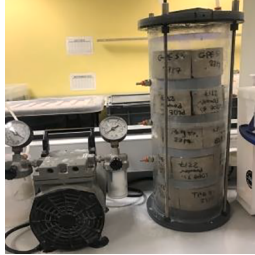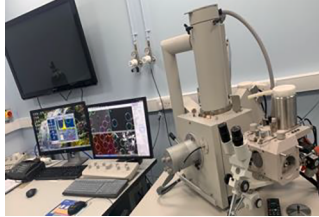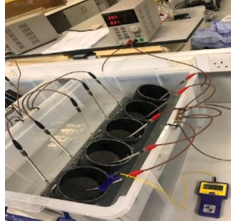

Fig. 6. (a) Materials required for one batch of concrete (1) OPC, (2) sand, (3) aggregate 10 mm, (4) aggregate 20 mm, (5) w/c 0.4; (b) casted concrete cubes and cylinders; (c) wet curing.

Table 4

Tests of the polymer modified concretes, with/without bioproduct (Plain, TPE, LDPE, PCL).

Test	Procedure/standard	Picture	Testing days
Slump	BS EN 12350-2:2009 [45]. The consistency of fresh concrete was analysed for all concrete mixtures.		0
Compressive strength	BS EN 12390-3:2019 [46], in 100 mm concrete cubes. The cubes were loaded to failure, in compliance with EN 12390-4 [47].		7, 14, 28, 60
Water absorption via capillary	BS EN 1015-18: 2002 [48].		28
Open porosity	BS EN 1936: 2006 [49]. Detailed description is presented below (Eq. (1)).		28, 48,60
Scanning electron microscopy (SEM)/EDS	FEI Inspect S SEM variable vacuum. Kv range 0.1–30 kv used		28
Non-steady state chloride migration	NT BUILD 492 [50]. Detailed description is presented below (Eq. (2)).		28, 60
Electrical resistivity of concrete	Four-point (Wenner probe) technique. Detailed description is presented below.		28, 60

Further experiments carried out to evaluate the mechanical and durability properties of concrete at various ages are summarised in Table 4.

2.7.2. Slump test

This research study recorded slump test results, a way to assess the consistency of fresh concrete, following to BS EN 12350-2:2009 [45], for all concrete mixtures during casting.

The test was performed by filling the slump cone in three equal layers and tamping down the mixture 25 times for each layer then the cone was raised upright. The difference in height between the cone and the concrete is the consistency of the slump (slump value in mm) (see Fig. 4.9). The slump test is sensitive to changes in concrete consistency between a slump value of 10 and 220 mm, enabling us to classify concrete using different consistency classes following BS EN 206-1 [51].
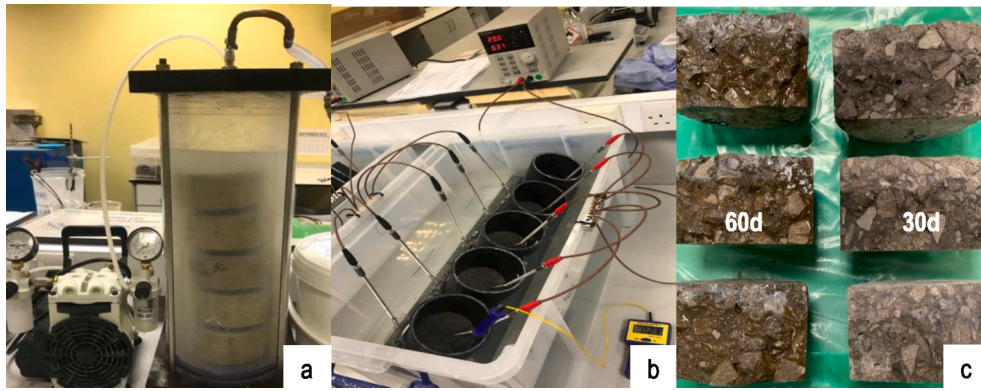
Fig. 7. (a) Samples Preconditioning in the vacuum; (b) applied voltage for 24 h; (c) chloride penetration depth in TPE + 0.5L Bio at 30 and 60 days.
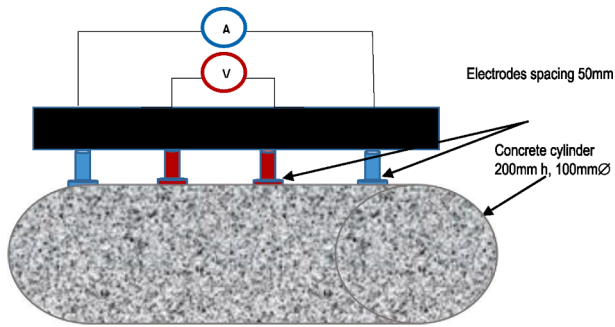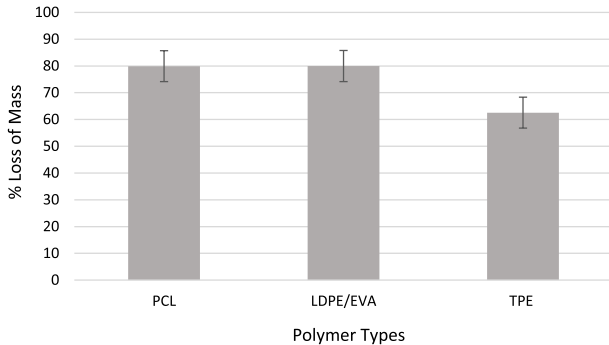

Fig. 8. Wenner four probe meter.

Fig. 9. Water loss analysis for polymers after 96 h at 40 °C.
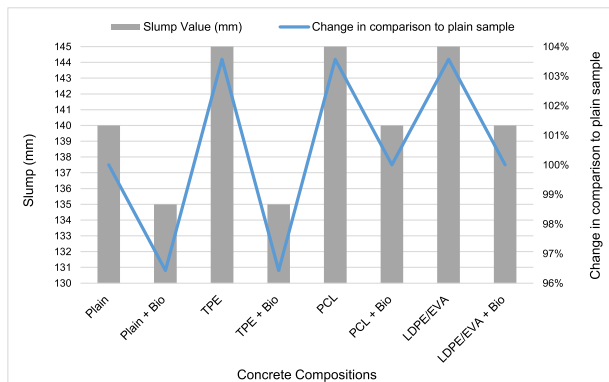

Fig. 10. Slump values for plain concrete, concrete with polymers and concrete with polymer plus bacteria.
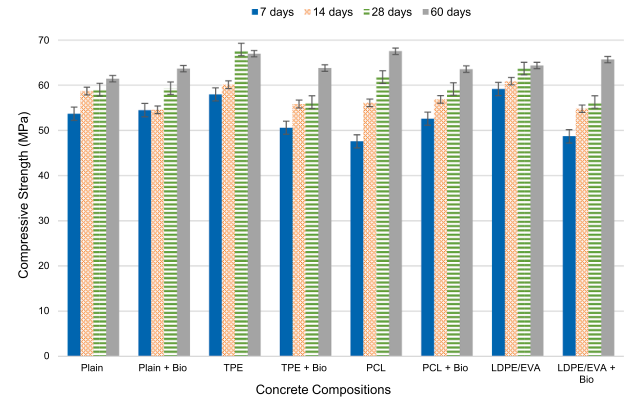
Fig. 11. Overall compressive strength results at 7, 14, 28 and 60 days, for plain concrete, concrete + polymers and concrete + polymer + bacteria.
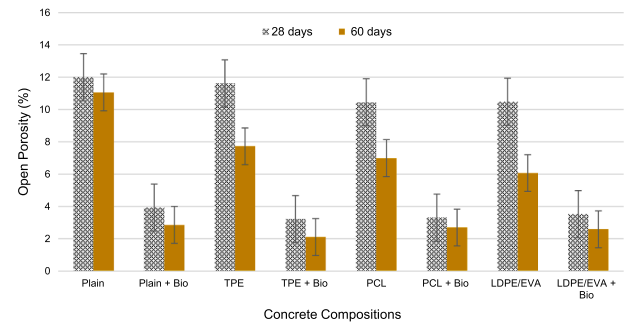
Fig. 12. Open porosity test for plain concrete, concrete + polymers and concrete + polymer + bacteria at 28 and 60 days.

2.7.3. Water absorption via capillary

Capillary test was carried out as per EN 1015-18:2002 [48]. Samples were placed in an oven at 70 °C to dry for a period of 8 days until the mass change was less than 0.1%. The concrete cylinders with 50 mm thickness were placed in 5 mm of water over the absorbent paper within an airtight container to keep hydrothermal conditions consistent as shown in Table 4. The weight of the samples was registered at 0′, 5′, 15′, 30′, 1 h, 2 h, 3 h, 21 h up to 28 days, until the water absorption reached the asymptotic value.

2.7.4. Open porosity test

The open porosity test, BS EN 1936:2006 [49], was used to conduct the test. The following Eq. (1) is used to calculate the volume percentage of open porosity in concrete specimens.

Fig. 13. Microstructure analysis of plain concrete.

$$OpenPorosity = \frac{M_3 - M_1}{M_3 - M_2} \times 100 \qquad (1)$$

where *M1* is the mass (g) of the sample after drying, *M2* is the mass (g) of the sample in hydrostatic circumstances (saturated and submerged in water), and *M3* is 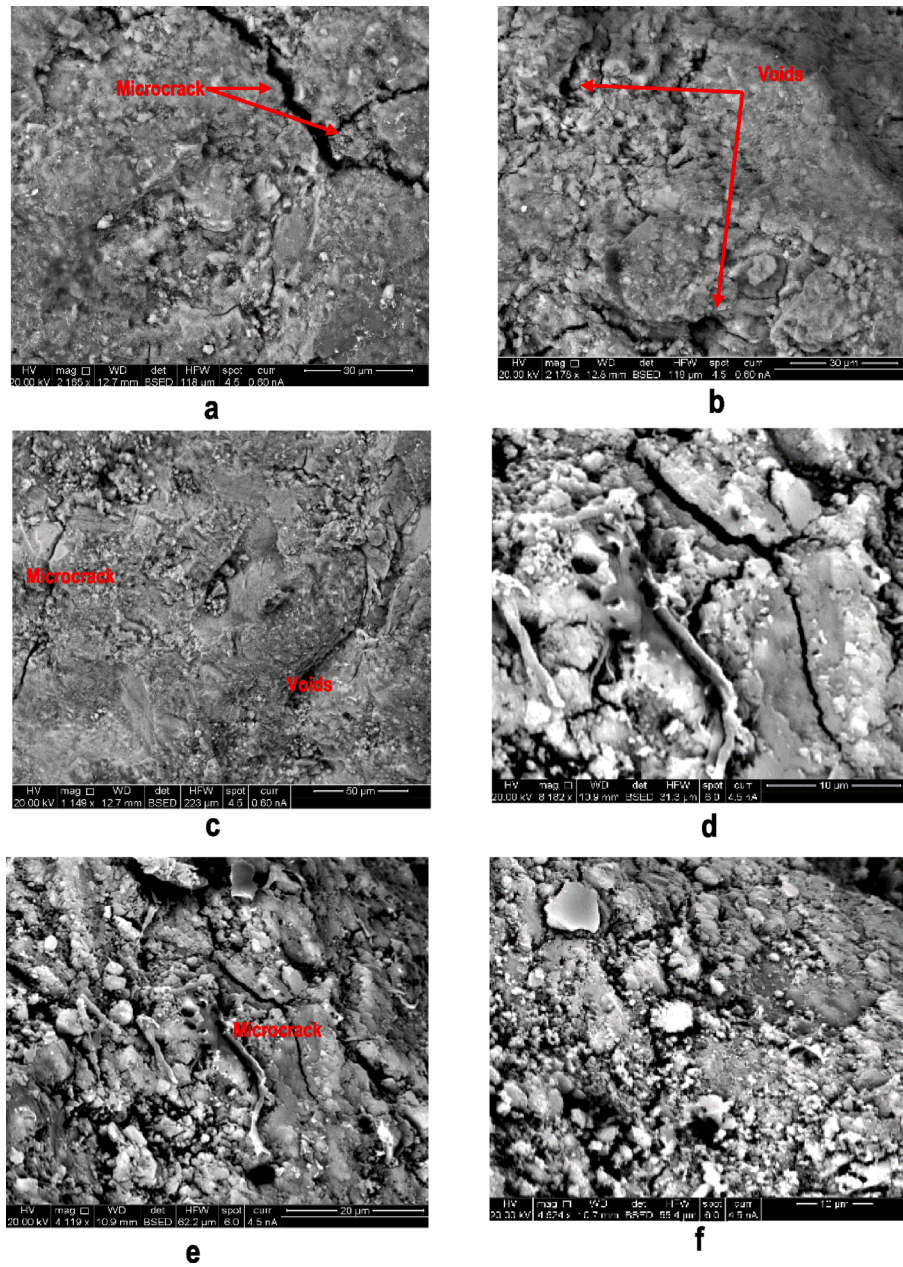the mass (g) of the sample saturated with water. The cylinder samples, each measuring 100 mm in diameter and 50 mm in length, were sliced into four parts, three of which were used for each composition.

2.7.5. Non-steady state chloride migration

The chloride migration experiment was conducted as per the NT BUILD 492 standard [50], and measurements were taken at 28 and 60 days for all samples (plain concrete, plain + polymer and plain + polymer + bacteria) with a thickness of 50 mm and a 100 mm diameter. Concrete cylinder samples were vacuumed for 3 h before being flooded with a saturated Ca(OH)$_2$ (calcium hydroxide) solution; the samples were then vacuumed for another 18 ± 2 h, as shown in Fig. 7(a). After

preconditioning, the concrete cylinders were firmly sealed in rubber sleeves, exposing only the bottom and top faces. The top face, which was exposed to a 0.3 NaOH (sodium hydroxide) anolyte solution, and the bottom face, subjected to a 10% NaCl (sodium chloride) catholyte solution (by mass), see Fig. 7(b). The power supply was connected to the entire system; at first, 30 V was applied, then the current was measured, and the ultimate V was set for 24 h. Using a hydraulic compression machine, the concrete specimens were split axially to assess chloride penetration into the samples. A silver nitrate solution was sprayed on the surface to measure the chloride penetration depth Fig. 7 (c).

Subsequently, the measurements were calculated using Eq. (2), where D$_{nssm}$ is the coefficient of migration ($\times 10^{-12}$ m^2/s), T, is the initial and final temperature (average) of the anolyte and catholyte solution, L, is the thickness of the concrete cylinder sample, U voltage applied, t is the duration of the test (hour), and xd is the average value of seven penetration depth in mm.
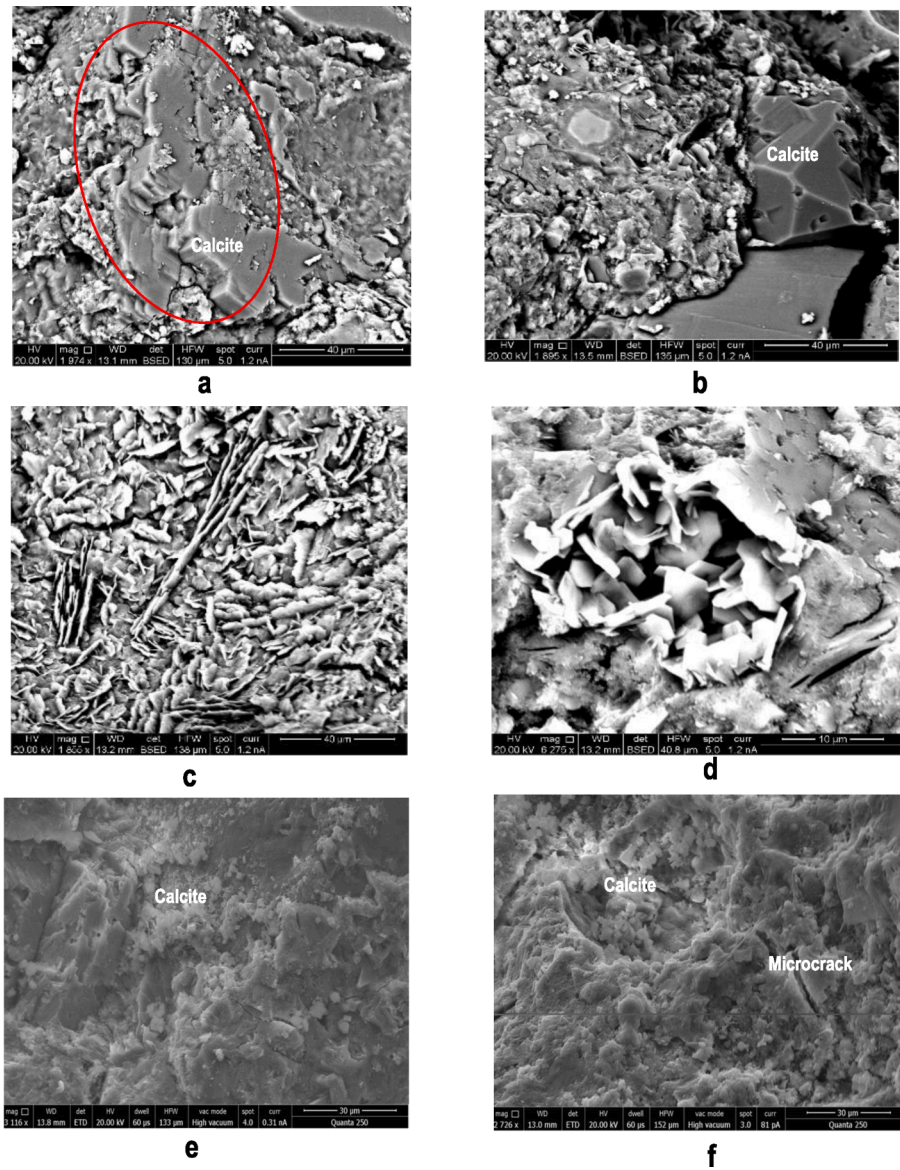
Fig. 14. Microstructure analysis for plain bio-concrete.

$$D_{nssm} = \frac{0.0239(273 + T)L}{(U - 2)t}\left(x_d - 0.0238\sqrt{\frac{(273 + T)Lx_d}{U - 2}}\right) \qquad (2)$$

2.7.6. Surface electrical resistivity

The surface electrical resistivity is an indicator of the permeability of concrete, and the test can be used to evaluate the performance of concrete. The overall purpose of most electrical resistivity approaches is to quantify the conductive characteristics of the concrete microstructure. Generally, concrete's electrical resistivity can be defined as its ability to tolerate the transfer of ions when exposed to an electrical field. Resistivity measurements can be utilized to determine the size and extent of pore interconnectivity in this situation [52].

The key elements impacting the electrical conductivity of concrete are including w/c ratio, sample age, proportion of pores and their size/distribution/connectivity in concrete, saturation level, pore fluid conductivity, and method of curing. The measurements can also be influenced by the electrode contact characteristics and the signal frequency [52].

Within this research study, the surface electrical resistivity of concrete was measured using a Resipod Wenner four probe meter. While the four electrodes are evenly spaced (50 mm) in a straight line when the outer electrodes apply current (A) to the concrete, and the two interior electrodes measure the electrical potential (V) produced see Fig. 8.

3. Results and discussion

3.1. Water loss analysis of polymers

The results presented in Fig. 9 shows that the majority of polymers when exposed for 96 h at 40 °C, lose absorbed water. However, for TPE the water seems to escape slower, emphasising the existence of higher chemical bonding with water. In general, TPE has a rougher surface, which increases the area of polymer in direct contact with water. The molecular weight tends to affect the surface tension of polymers. For polymers with high molecular weight this effect can be neglected, but not for polymers with low molecular weight. In comparison to other polymers, TPE present a low molecular weight, which is associated with a low diffusion rate and might explain this behaviour.
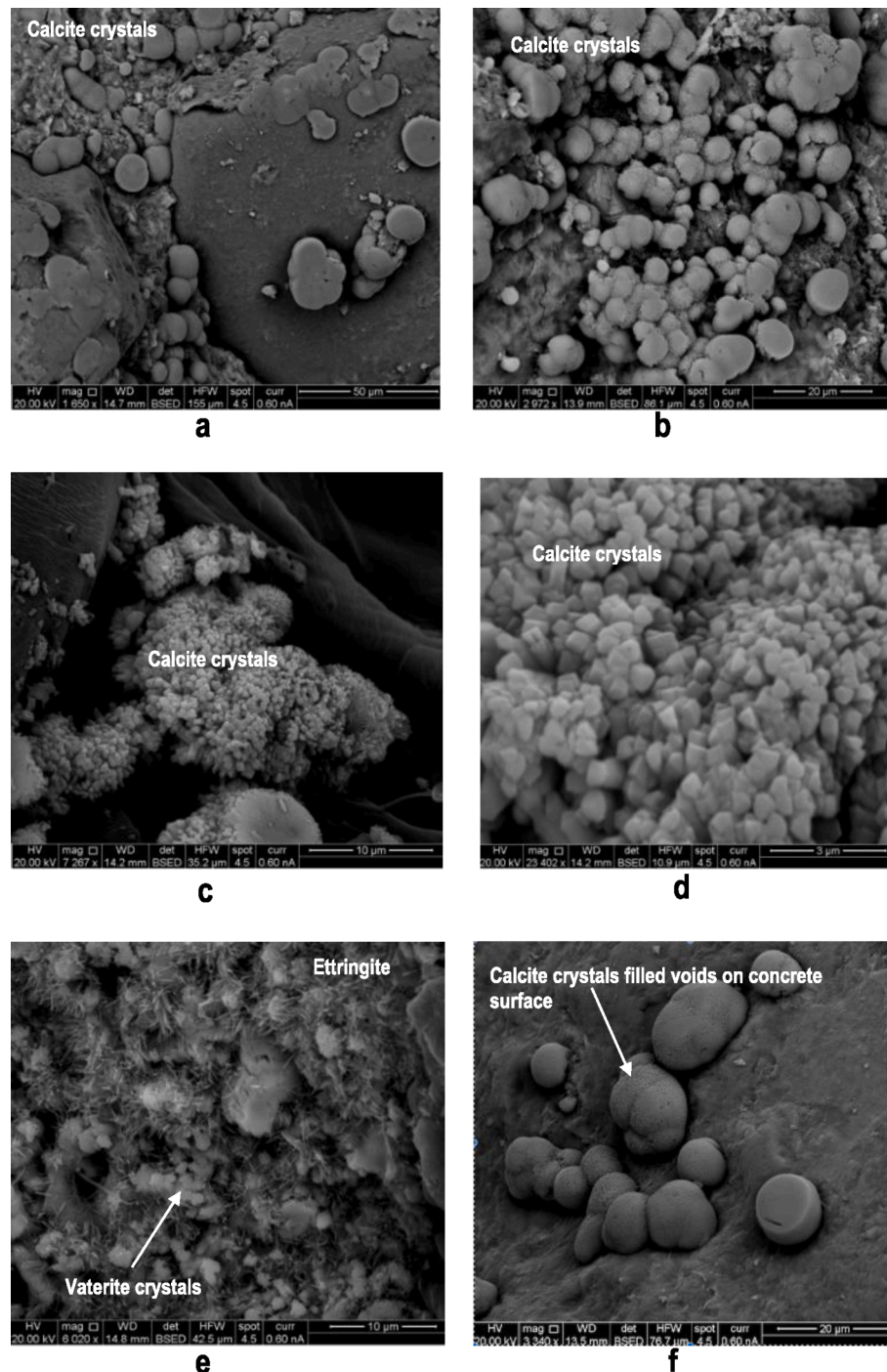
Fig. 15. Microstructure analysis for LDPE/EVA bio-concrete.

3.2. Slump test

The hardened state properties of concrete are highly dependent on its workability. The slump test was performed to quantify the effect of the microbial self-healing agents on the workability of fresh concrete. Fig. 10 shows that 3% polymer modified concrete leads to an improvement in slump of 4% in comparison to a plain sample, which corresponds to a consistency class of S3, enabling the concretes to be used for normal RC, manually compacted, and heavily reinforced sections with vibrations.

This slump increase in comparison to plain concrete composition is explained by the small size and smooth surface of the polymers when compared to sand. According to Sakia and de Brito [52], polymer form and surface texture have a direct impact on fresh concrete. In the case of TPE + bio, the use of bioproducts in polymer-modified concrete tends to slightly decrease the slump to values similar to those of plain concrete. For PCL + Bio and LDPE + Bio concrete compositions, the slump results are slightly smaller than for polymer concrete without bioproducts. This means that the slump results with the use of bioproduct are still very competitive, leading only to a small modification of the workability of concrete.
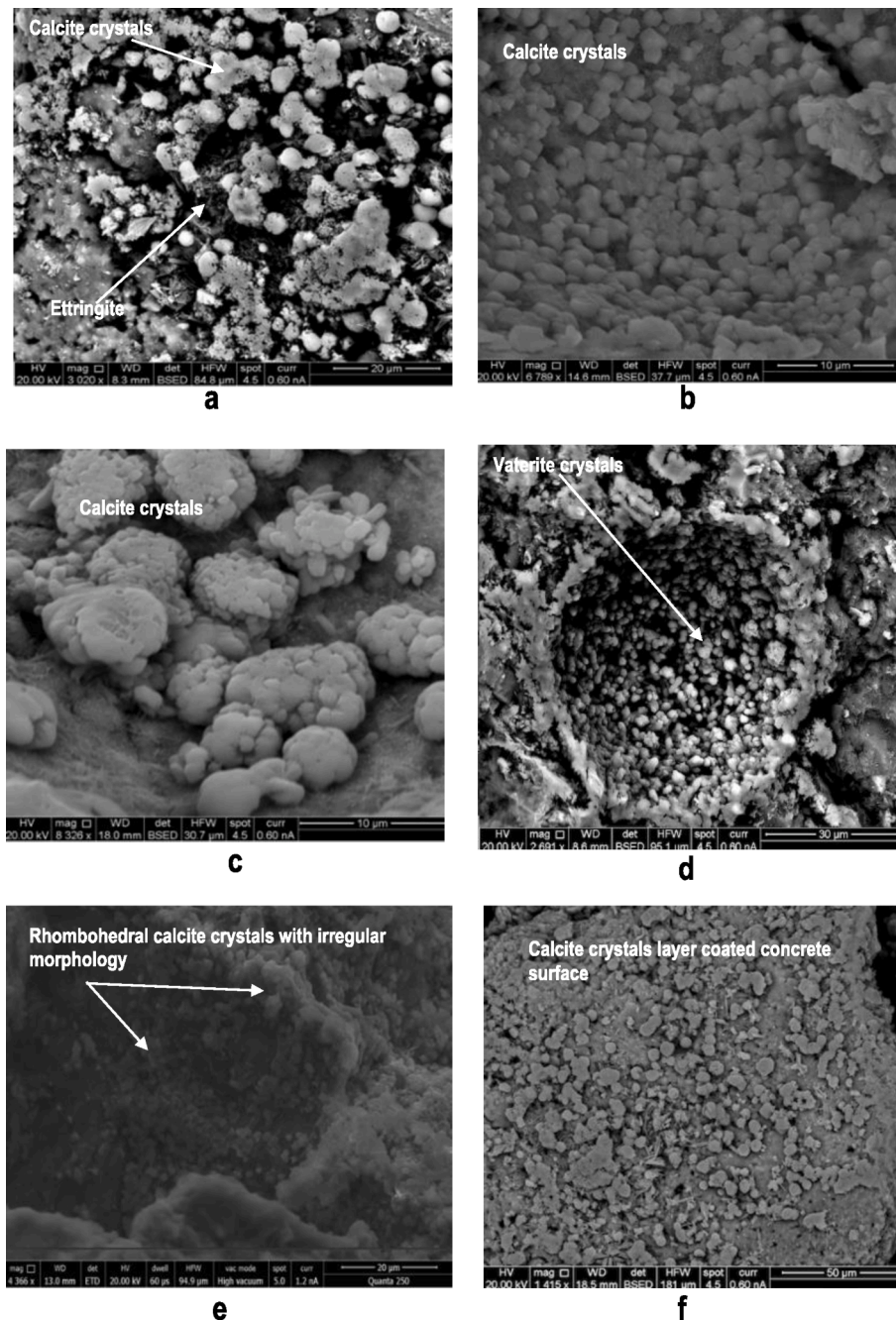
Fig. 16. Microstructure analysis for TPE bio-concrete.

3.3. Compressive strength

Fig. 11 shows the compressive strength results at 7, 14, 28 and 60 days, for all three groups of concrete, including plain, plain + polymer, and plain + polymer + bacteria.

It can be shown that the use of bioproducts tends to delay the increase in compressive strength with time, especially until the 14 days. However, despite the fact that the 28-day results are not yet at the same level as the ones obtained for the polymer-modified concrete compositions, the compressive strength results for the concretes with bioproduct seem to keep growing and eventually reach a similar level to the ones without bioproduct.

At 60 days, all polymer-modified concrete reaches more than 60 MPa of compressive strength, no matter if a bioproduct is added or not, except for LDPE, where the addition of a bioproduct substantially increases the compressive strength to 67 MPa.

Adding the bioproduct to the plain concrete composition leads to similar 28-day strengths, even though at 14 days the results are lower than for the plain composition. This might be associated with a delay in cement hydration due to the presence of a bioproduct.

At 28 days, the highest compressive strength (68 MPa) is obtained if TPE is modified in the concrete, and despite TPE's lower density (0.88 g/cm^3), the coefficient of variation (COV) of concrete's compressive strength was only 2%.

At 28 days, TPE with bioproduct (COV = 4%) leads to a decrease in the concrete's compressive strength of 17%. With LDPE, the bioproduct leads to a decrease of 12% in the compressive strength, and for PCL, the decrease is only 4% in comparison to the concrete without the Bio. COV was very low for low density polymer-modified concrete (LDPE concrete presented a COV of 3%). COV is 7% for PCL concrete, a higher density
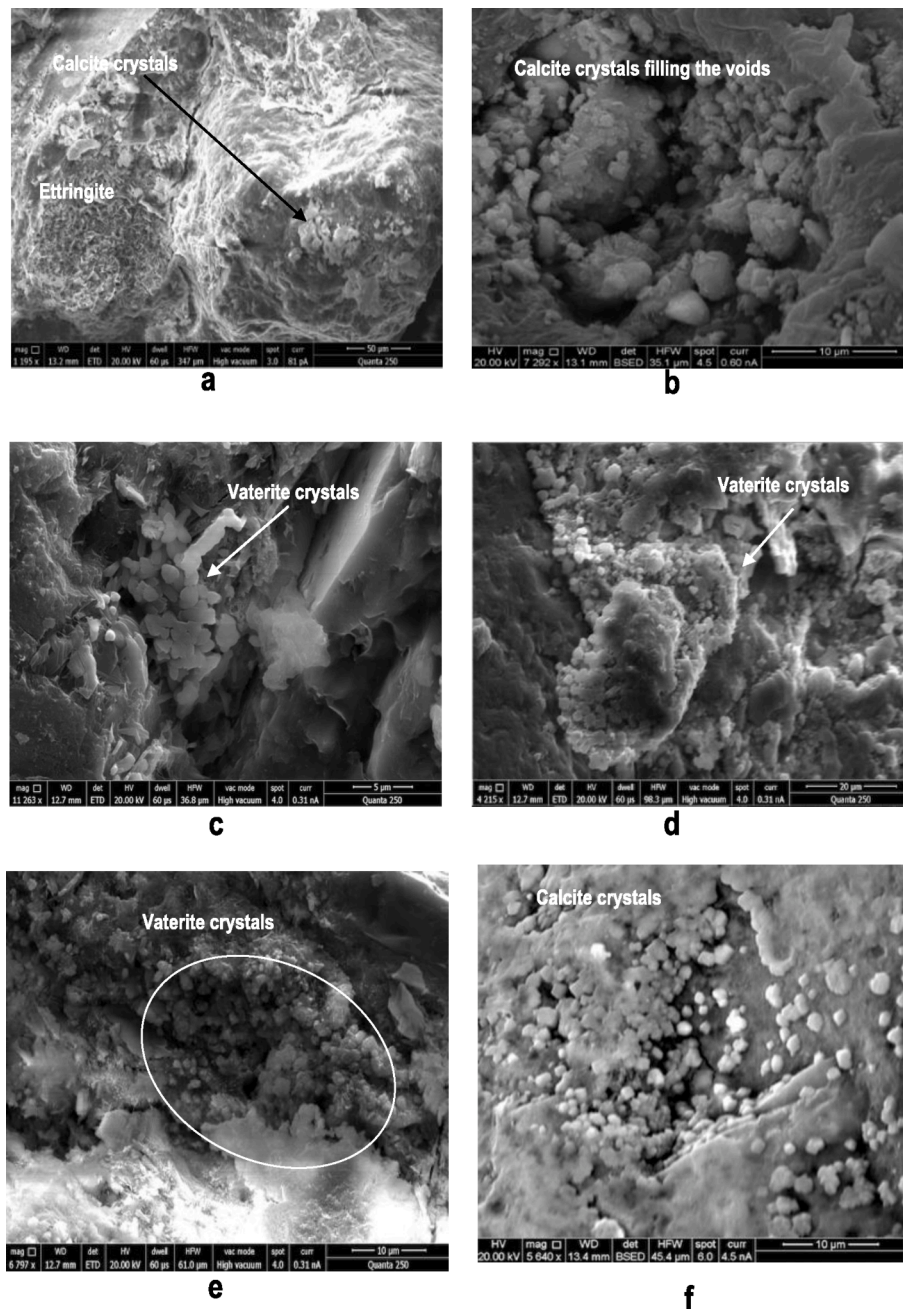
Fig. 17. Microstructure analysis for PCL bio-concrete.

polymer.

3.4. Porosity

The Fig. 12 presents the comparison between the porosity at 28 and 60 days for the concretes with polymer modification and the ones with an addition of bioproduct. At 28 days, the small amount of polymer decreases porosity up to 1% in comparison to plain concrete. However, the most impressive results happen if a bioproduct is added. The results show that the use of bioproducts leads to an impressive decrease in porosity, from 12 to 20%. This reduction in the quantity of concrete pores will probably be associated with a reduction of capillary suction (related to pores' transport of O_2 and CO_2) and diffusion (related to the transport of water and ions as chloride).

At 60 days, all concrete compositions modified with polymer decrease the porosity to values of around 3–4%. The bioproduct accelerates that decrease in a more effective way than polymers, which is probably associated with a densification of the concrete matrix due to biomineralisation. The pore size distribution and the form of the interconnections has a significant impact on its durability of concrete. Permeability is reduced when the pore network is finer and less connected. On the other hand, a porous microstructure with a higher degree of interconnectivity results in higher permeability and, in general, worse durability.

As a result of this research, it was demonstrated that microbially produced calcium precipitation has the ability to significantly inhibit water penetration through concrete.

3.5. SEM/EDs

To establish the production and crystal structure of $CaCO_3$ induced by *Shewanella*, microscale inspection of precipitated crystals was carried
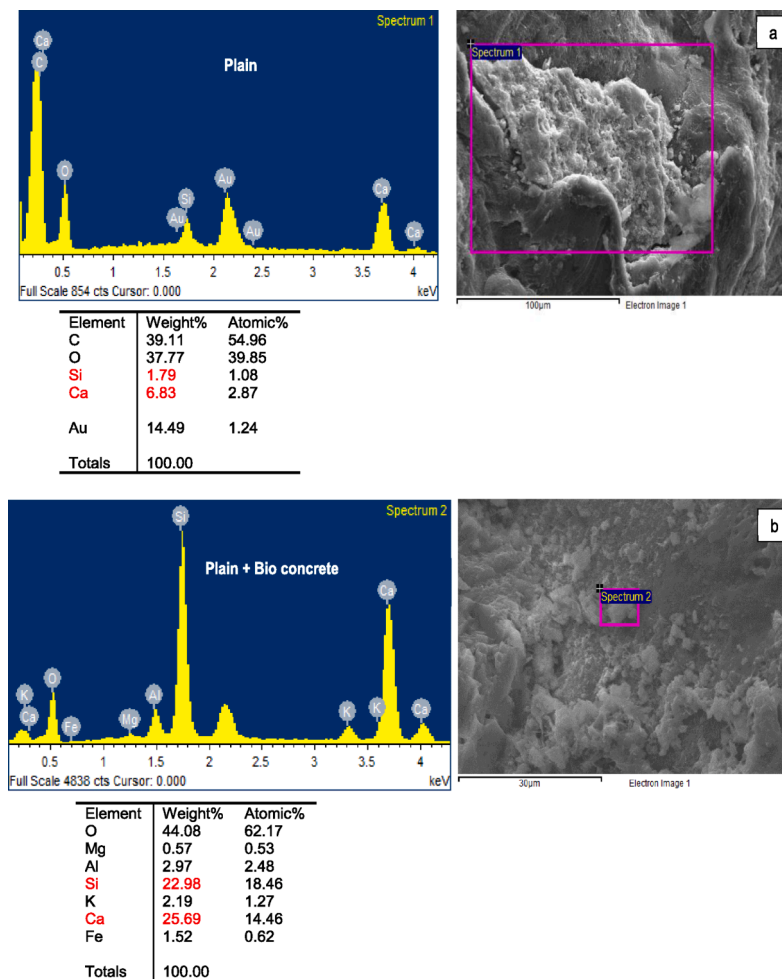
Fig. 18. (a, b, c, d, e) presents the EDX data for plain, plain + bio, and polymer modified bio concrete (TPE, LDPE/EVA, PCL).

out using SEM. The inner part of each concrete sample was coated in gold to investigate the surface of the paste and the aggregates with or without the bioproduct. At 28 days, plain, plain with bio, and polymer-modified bio-concrete specimens were scanned electronically. The microstructure analysis of the samples is illustrated in Figs. 14, 14, 15, 16, and 17. Fig. 13(a, b, c, d, e, f) shows the SEM analysis of a plain concrete sample with visible microcracks and voids. Fig. 14(a, b, c, d, e, f) demonstrates the micro-structure of plain bio-concrete, which reveals the existence of crystalline $CaCO_3$, which correlates with bacteria precipitation; nearly all microcracks and voids are filled with calcite, with only a little microcrack visible in Fig. 14(f).

According to the SEM micrographs of the precipitated crystals, different morphologies of $CaCO_3$ (calcite, aragonite and vaterite) can be formed by the bacteria. The $CaCO_3$ minerals formed by bacteria are microbial induced calcium precipitation, generally calcite [53]. The SEM micrographs revealed that vaterite and calcite were the most frequent morphologies produced by candidate bacteria. Figs. 15, 16 and 17 display the micrographs of polymer-modified bio-concrete (LDPE/EVA, TPE and PCL). The existence of tetrahedron and pyramid structures in polymer modified bio-concrete indicates that calcite is present. This means that the concrete pores are filled with deposited calcite, which increases the strength and durability of the concrete. Calcite deposition is used to provide a barrier against harmful substances, which enhances the mechanical properties and permeability of concrete.

Figs. 14, 15, 16, and 17 illustrate the bio-mineralisation products that are densely stacked, and they compactly filled the concrete cracks. However, different $CaCO_3$ polymorphs have a range of stabilities.

Calcite is thermodynamically the most stable and the most common polymorph, while aragonite is relatively less stable and vaterite is only metastable, it might change to calcite or aragonite [54]. Calcite crystals have a rhombohedral structure whereas vaterite and aragonite crystals have a hexagonal and orthorhombic (needle-like) structure [55]. Calcite and vaterite are the main phases at lower temperatures, while aragonite precipitates at higher temperatures, particularly around 60 °C. As a result, calcite and vaterite were anticipated to be the two ultimate polymorphous compositions in this research investigation as all exposure circumstances were $\geq$40 °C [56]. Vaterite and calcite are precipitated in a pH $\geq$12 and aragonite formed at a lower pH [55]. Crystal size also affects stability. Larger calcite crystals are generally more stable and are often rounded when precipitated in the presence of microorganisms. Spherical crystal morphology would be expected to improve the rheological properties of bio-concrete. SEM analysis of bacterial concrete samples revealed spherical calcite crystals in bio-TPE, and bio-LEPE/EVA modified concrete, as shown in Fig. 15 a and b, and 16b, c, and d, respectively. Bio-LDPE/EVA (Fig. 15b), bio-TPE (16c and d), and bio-PCL (Fig. 17f) modified concrete also contained rhombohedral polymorph crystals.

EDS at 15.0 keV was used to further characterise the bio-precipitates. It is used as an analytical approach to detect the elements included in the formed crystals. The number of elements in a sample can be measured by the intensity of peaks, which are identified by atomic %. To determine the elemental ratio of $CaCO_3$, EDS was performed for the same concrete pieces as for SEM analysis. From EDS analysis, the amount of Ca acquired for bacterial concrete is higher than in plain concrete. However,
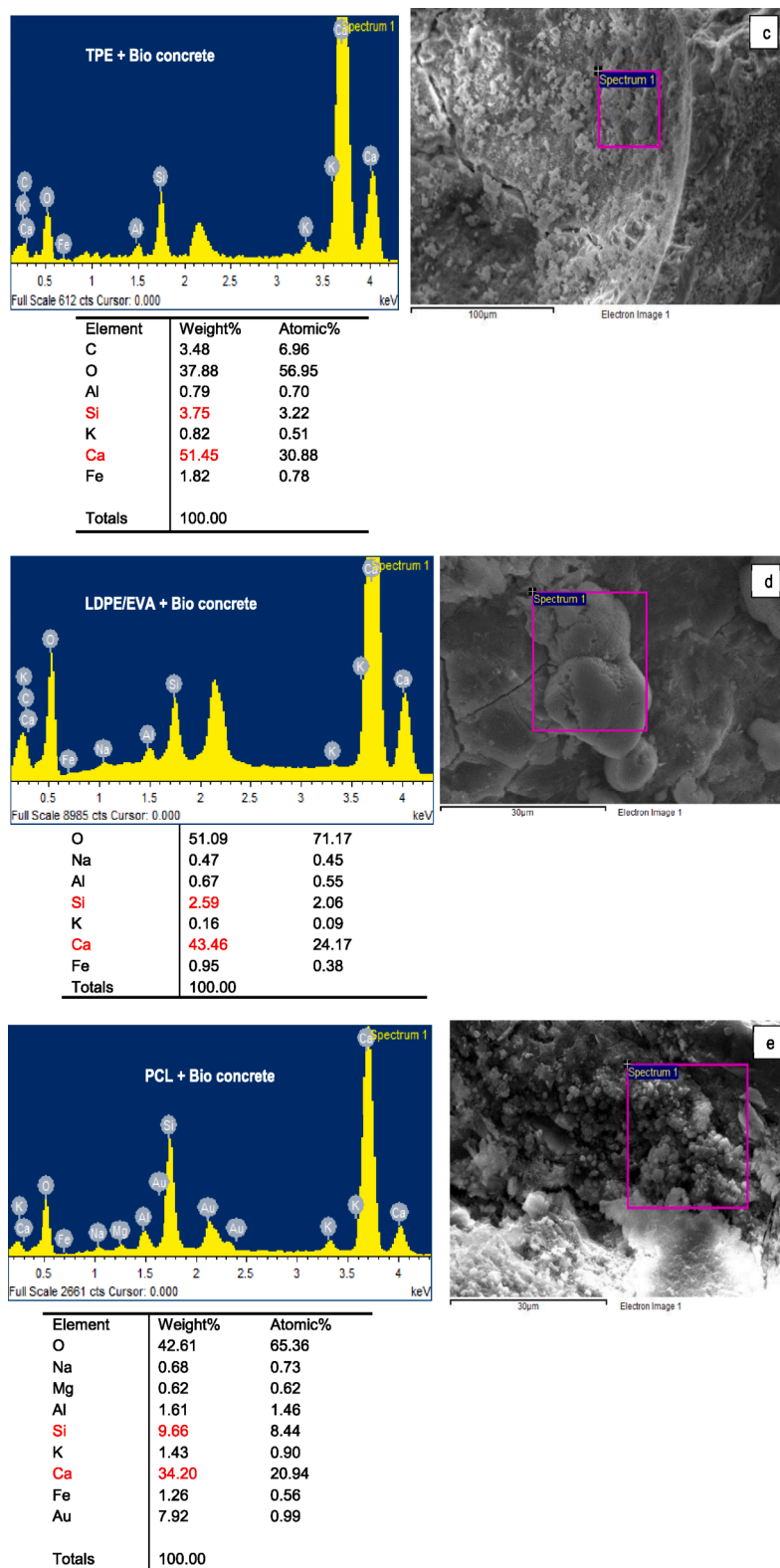
TPE + Bio concrete

Element	Weight%	Atomic%
C	3.48	6.96
O	37.88	56.95
Al	0.79	0.70
Si	3.75	3.22
K	0.82	0.51
Ca	51.45	30.88
Fe	1.82	0.78
Totals	100.00	

LDPE/EVA + Bio concrete

	Weight%	Atomic%
O	51.09	71.17
Na	0.47	0.45
Al	0.67	0.55
Si	2.59	2.06
K	0.16	0.09
Ca	43.46	24.17
Fe	0.95	0.38
Totals	100.00	

PCL + Bio concrete

Element	Weight%	Atomic%
O	42.61	65.36
Na	0.68	0.73
Mg	0.62	0.62
Al	1.61	1.46
Si	9.66	8.44
K	1.43	0.90
Ca	34.20	20.94
Fe	1.26	0.56
Au	7.92	0.99
Totals	100.00	

Fig. 18. (*continued*).

as shown in Fig. 18(a, b, c, d, e), the amount of Ca in polymer-modified bio-concrete is significantly higher than in plain bio-concrete. The existence of a larger amount of Ca in bacterial concrete is confirmed by elemental analysis. The presence of $CaCO_3$ in bacterial concrete is confirmed by SEM and EDS tests. This improves the strength and durability of concrete by filling pores and microscopic voids. The high

calcium amounts in the bacterial samples prove that calcite was present in the form of $CaCO_3$ due to the presence of bacteria.

3.6. Water absorption via capillary

The capillary test reveals that the healing-agent leads to a significant
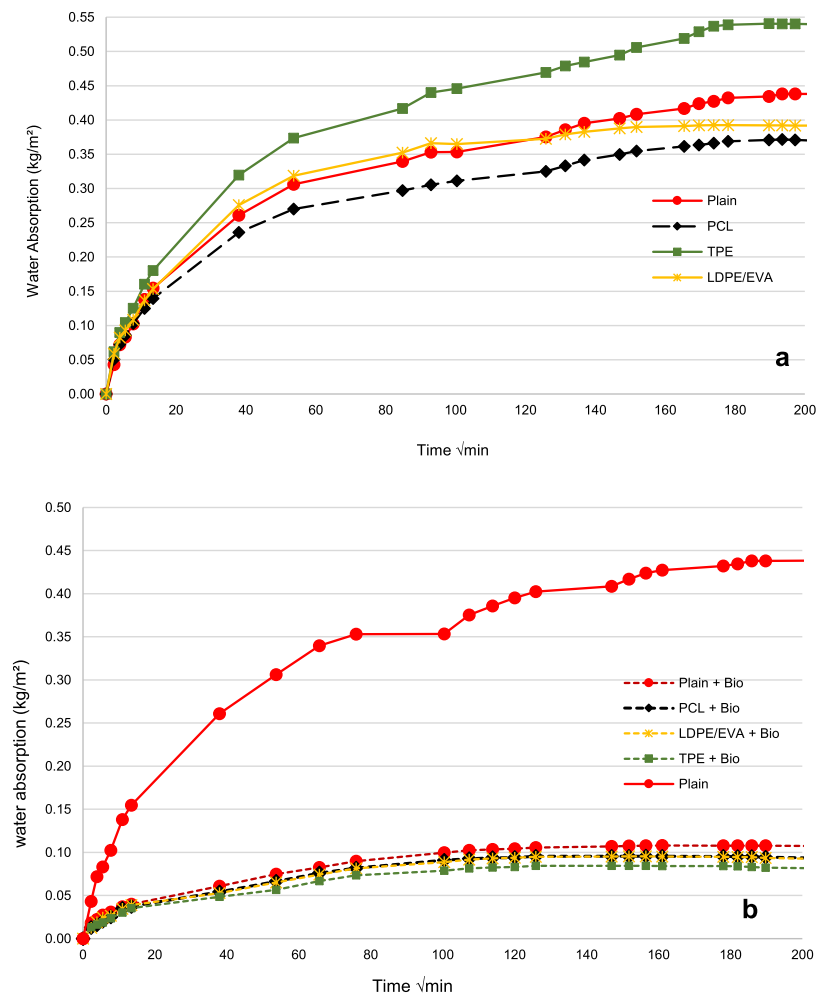
Fig. 19. a: Water absorption for plain concrete and polymer modified concrete; b: Water absorption for plain + bio; polymer modified concrete with bioproduct and comparison to Plain.
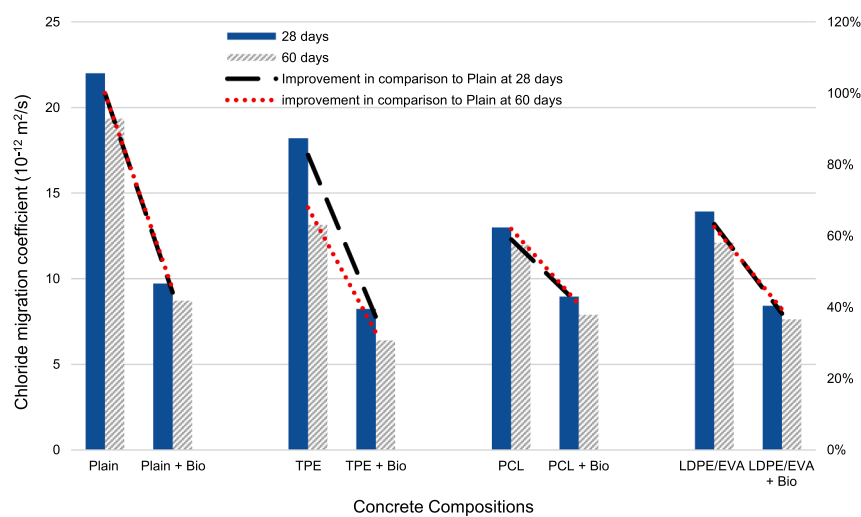
Fig. 20. Chloride migration coefficient of concrete with and without the bioproduct at 28 and 60 days.

reduction in the water absorption in all concretes, including the plain composition. The results show that the bio-product plays a dominant role in the control of capillaries and prevents water migration more

effectively in comparison to the use of different polymers in concrete, as the results tend to be similar (except for TPE concrete, where absorption is higher as TPE is a porous type of polymer with increased water
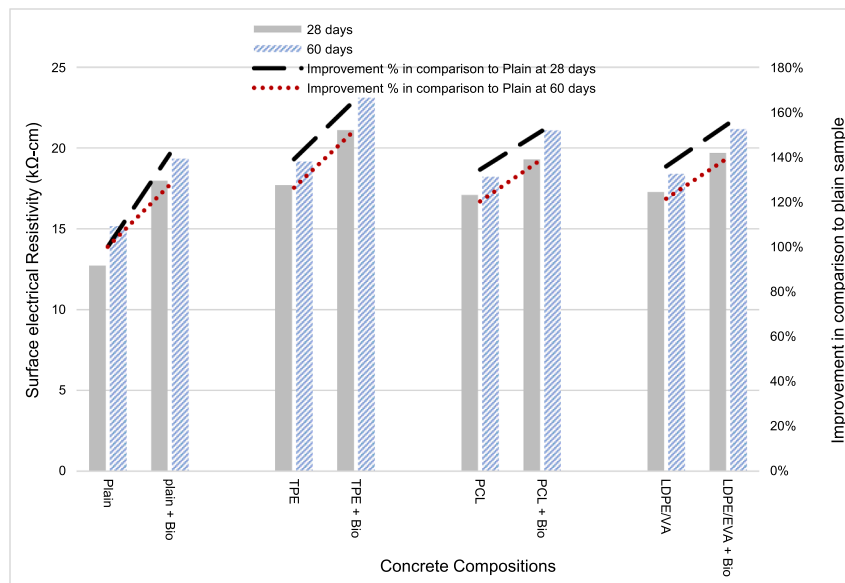
Fig. 21. Surface electrical resistivity measurement at 28 and 60 days.

permeability (see Fig. 19a) [14]. After two days of exposure to water, all concretes mixed with the bio-product and polymers significantly prevented water migration, highlighting the effectiveness of the bacteria precipitation, which was able to stabilise and decrease the maximum absorbed water by 85% in comparison to plain concrete (Fig. 19b). The first seven days are responsible for almost 100% of the absorption of water by all concrete and stabilisation of its mass. TPE + bio-concrete composition tends to absorb less water than the others. The reduction of water absorption via capillaries is associated with less transport of O_2 and CO_2, contributing to minimising the risk of corrosion in RC.

The SEM/EDS discussed above confirms that the presence of bacteria that contribute to $CaCO_3$ generation resulted in a marked reduction of water absorption (Fig. 19b) when compared to plain specimens.

3.7. Chloride migration coefficient

Fig. 20 illustrates the results of the chloride migration coefficient for plain concrete, polymer-modified concrete (TPE, LDPE, and PCL) with and without bioproduct for 28 and 60 days of aging. For sand replacement with 3% of polymer, the chloride migration coefficient can decrease by 20 to 40%. At 60 days, all polymers lead to a similar decrease in the coefficient of migration in the concrete, to values around 12×10^{-12} m^2/s.

However, in agreement with the previous results of porosity and capillary, when a bioproduct is used, migration of chlorides decreases by an average of 60%, reaching values of 7×10^{-12} m^2/s in comparison to plain concrete, no matter the type of polymer used in the concrete. It seems that the bioproduct can minimise the migration of chlorides, a water-soluble ion, in wet or humid concrete porous medium environments but also in low relative humidity environments, as happens when the concrete is exposed to capillary suction.

3.8. Electrical resistivity

Fig. 21 displays the results of surface electrical resistivity for plain, plain + polymer, and plain + bioproduct with and without the bioproduct. At 28 days, the electrical resistivity of concrete improved by 40% with the addition of polymers compared to a plain sample. Furthermore, as seen in the figure, employing bacteria increased the electrical resistance of both plain and polymer-modified concrete. Plain concrete with bacteria improved by 40%, while polymer bio-concrete improved by 66%. The highest electrical resistivity values have been

recorded in TPE bio-concrete. Having higher surface electrical resistivity in bacterial samples compared to the plain, it is possible to conclude that the production of calcite deposits in the concrete pores reduces the fluid conductivity and increases the electrical resistivity of the concrete pores. Therefore, the results are consistent with the chloride migration coefficient: the lower the chloride migration coefficient, the higher the surface electrical resistance.

4. Conclusions

This research work intends to compare the performance of three types of polymer-modified concrete (TPE, LDPE/EVA, and PCL) if bacteria-based solutions are used for reinforced concrete (RC) structures designed for a compressive strength higher than 50 MPa. The aim was to comprehend the impact on concrete's final mechanical and durability performances. The work shows that:

It is possible to incorporate thermoplastic polymers into concrete to increase the strength and electrical resistance and decrease chloride migration. However, the use of bioproducts is crucial to creating a drop in the open porosity values between 28 and 60 days, from 12% to 4%.

At early stages, the concrete with PCL benefits from the use of bioproduct, as the compressive strength easily reaches 50 MPa at 7 days. However, the use of bioproducts tends to delay the increase of concrete's compressive strength with time, especially until the 14 days. At 28 days all concretes present values above 55 MPa. For LDPE, the addition of bioproduct substantially increases the compressive strength to 67 MPa.

The microstructure analysis shows that the microcracks detected in the plain concrete at 28 days are not observed in the polymer-modified concrete with bioproduct. The presence of bacterial $CaCO_3$ precipitation is revealed by SEM/EDX. The existence of tetrahedron and pyramid structures in polymer modified bio-concrete indicates that calcite is present and that the quantity of calcium carbonate in the polymer-modified bio-concrete is significantly higher than in plain bio-concrete or even plain.

In comparison to the usage of various polymers in concrete, the bioproduct (bacteria) plays a significant role in the control of concrete capillary and efficiently prevents water migration. The first seven days are responsible for almost 100% of the absorption of water by all concrete and stabilisation of its mass. TPE + bio concrete composition tends to absorb less water than the others.

The migration of chlorides decreases by an average of 60% in comparison to plain water, reaching values of 7×10^{-12} m^2/s no matter the

type of polymer used in the concrete.

The highest electrical resistivity values have been recorded by TPE bio-concrete. Having a higher surface electrical resistivity of bacterial samples compared to the plain, it is possible to conclude that the production of calcite deposits in the concrete pores reduces the fluid conductivity and increases the electrical resistivity of the concrete pores.

CRediT authorship contribution statement

Hazha Mohammed: Methodology, Data curation, Investigation, Writing – original draft. **Francesca Giuntini:** Methodology, Writing – original draft, Writing – review & editing, Investigation, Validation. **Alan Simm:** Writing – review & editing, Validation. **Monower Sadique:** Writing – review & editing, Validation. **Andy Shaw:** Writing – review & editing, Validation. **Ismini Nakouti:** Writing – review & editing, Validation. **Ana Bras:** Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

References

[1] M.D. Anderson, et al. Polymer-Modified Concrete ACI 548. 3 R-03 Reported by ACI Committee 548. 2003.

[2] Z. Li, et al., Advanced Concrete Technology, John Wiley & Sons, 2022.

[3] L. Czarnecki, Polymer-concrete composites for the repair of concrete structures, MATEC Web Conf. 199 (2018) 01006.

[4] W.J. Lewis, G. Lewis, The influence of polymer latex modifiers on the properties of concrete, Composites 21 (6) (1990) 487–494.

[5] R. Deshrousses, A. Soliman, The uses of polymers in concrete: potentials and difficulties, Building Tomorrow's Society, 2018, https://csce.ca/elf/apps/CONFERENCEVIEWER/conferences/2018/pdfs/Paper_MA63_0610040527.pdf6. S. M. Malkapur, et al., Waste-polymer incorporated concrete mixes for neutron and gamma radiation shielding. Progr. Nuclear Energy, 135 (2021) 103694.

[6] F. Pacheco-Torgal, Y. Ding, S. Jalali, Properties and durability of concrete containing polymeric wastes (tyre rubber and polyethylene terephthalate bottles): An overview, Constr. Build. Mater. 30 (2012) 714–724.

[7] N. Saikia, J. de Brito, Use of plastic waste as aggregate in cement mortar and concrete preparation: A review, Constr. Build. Mater. 34 (2012) 385–401.

[8] M.A. Yahya, The effect of polymer materials on the fracture characteristics of high-performance concrete (Hpc), in: School of Engineering and the Built Environment. 2015, Edinburgh Napier University: Edinburgh, Scotland, United Kingdom. p. 182.

[9] D.W. Fowler, Polymers in concrete: a vision for the 21st century, Cem. Concr. Compos. 21 (5–6) (1999) 449–452.

[10] L. Czarnecki, Polymer-Concrete Composites for the repair of concrete structures. MATEC Web Conf. 199 (2018) 01006. https://doi.org/10.1051/matecconf/201819901006.

[11] Z.Z. Ismail, E.A. Al-Hashmi, Use of waste plastic in concrete mixture as aggregate replacement, Waste Manag. 28 (11) (2008) 2041–2047, https://doi.org/10.1016/j.wasman.2007.08.023. Epub 2007 Oct 10 PMID: 17931848.

[12] S.B. Kim, N.H. Yi, H.Y. Kim, J.H.J. Kim, Y.C. Song, Material and structural performance evaluation of recycled PET fibre reinforced concrete, Cem. Concr. Compos. 32 (2010) 232–240, https://doi.org/10.1016/j.cemconcomp.2009.11.002.

[13] H. Mohammed, F. Giuntini, M. Sadique, A. Shaw, A. Bras, Polymer modified concrete impact on the durability of infrastructure exposed to chloride environments, Constr. Build. Mater. (2022), https://doi.org/10.1016/j.conbuildmat.2021.125771.

[14] S. Kane, A. Thane, M. Espinal, et al., Biomineralization of plastic waste to improve the strength of plastic-reinforced cement mortar, Materials (Basel) 14 (8) (2021) 1949, https://doi.org/10.3390/ma14081949. Published 2021 Apr 13.

[15] A. Bras, et al., Design service life of RC structures with self-healing behaviour to increase infrastructure carbon savings, Materials MDPI 14 (2021) 3154, https://doi.org/10.3390/ma14123154.

[16] H. Mohammed, M. Ortoneda-Pedrola, I. Nakouti, A. Bras, Experimental characterisation of non-encapsulated bio-based concrete with self-healing capacity, Constr. Build. Mater. 256 (2020), https://doi.org/10.1016/j.conbuildmat.2020.119411.

[17] J.M. van der Bergh, B. Miljević, S. Vučetić, O. Šovljanski, S. Markov, M. Riley, J. Ranogajec, A. Bras, Comparison of microbially induced healing solutions for crack repairs of cement-based infrastructure, Sustainability 13 (8) (2021) 4287, https://doi.org/10.3390/su13084287.

[18] W. De Muynck, N. De Belie, W. Verstraete, Microbial carbonate precipitation in construction materials: A review, Ecol. Eng. 36 (2010) 118–136, https://doi.org/10.1016/j.ecoleng.2009.02.006.

[19] N. De Belie, E. Gruyaert, A. Al-Tabbaa, P. Antonaci, C. Baera, D. Bajare, A. Darquennes, R. Davies, L. Ferrara, T. Jefferson, et al., A review of self-healing concrete for damage management of structures, Adv. Mater. Interfaces 5 (2018) 1–28, https://doi.org/10.1002/admi.201800074.

[20] V. Wiktor, H. Jonkers, Quantification of crack-healing in novel bacteria-based self-healing concrete, Cem. Concr. Compos. 33 (2011) 763–770, https://doi.org/10.1016/j.cemconcomp.2011.03.012.

[21] J. Xu, W. Yao, Multiscale mechanical quantification of self-healing concrete incorporating non-ureolytic bacteria-based healing agent, Cem. Concr. Res. 64 (2014) 1–10, https://doi.org/10.1016/j.cemconres.2014.06.003.

[22] K.A. Paine, M. Alazhari, T. Sharma, R. Cooper, Design and performance of bacteria-based self-healing concrete, in: Proceedings of the 9th International Concrete Conference 2016 Environment Efficiency Economic Challenges Concrete, 4 July 2016, Dundee, UK; pp. 545–554.

[23] H.M. Jonkers, A. Thijssen, G. Muyzer, O. Copuroglu, E. Schlangen, Application of bacteria as self-healing agent for the development of sustainable concrete, Ecol. Eng. 36 (2010) 230–235, https://doi.org/10.1016/j.ecoleng.2008.12.036.

[24] H. Afifudin, et al., Microorganism precipitation in enhancing concrete properties, Appl. Mech. Mater. (2011) 99–100.

[25] H.M. Jonkers, et al., Application of bacteria as self-healing agent for the development of sustainable concrete, Ecol. Eng. 36 (2) (2010) 230–235.

[26] S.-G. Choi, et al., Mortar crack repair using microbial induced calcite precipitation method, Cem. Concr. Compos. 83 (2017) 209–221.

[27] V. Wiktor, H.M. Jonkers, Field performance of bacteria-based repair system: Pilot study in a parking garage, Case Stud. Constr. Mater. 2 (2015) 11–17.

[28] R. Alghamri, A. Kanellopoulos, A. Al-Tabbaa, Impregnation and encapsulation of lightweight aggregates for self-healing concrete, Constr. Build. Mater. 124 (2016) 910–921.

[29] T. Zheng, et al., Effect and mechanism of encapsulation-based spores on self-healing concrete at different curing ages, ACS Appl. Mater. Interfaces 12 (47) (2020) 52415–52432.

[30] B. Van Belleghem, et al., Chloride induced reinforcement corrosion behavior in self-healing concrete with encapsulated polyurethane, Cem. Concr. Res. 113 (2018) 130–139.

[31] J. Wang, et al., Use of silica gel or polyurethane immobilized bacteria for self-healing concrete, Constr. Build. Mater. 26 (1) (2012) 532–540.

[32] D. Palin, V. Wiktor, H.M. Jonkers, Autogenous healing of marine exposed concrete: Characterization and quantification through visual crack closure, Cem. Concr. Res. 73 (2015) 17–24.

[33] J.Y. Wang, et al., Application of hydrogel encapsulated carbonate precipitating bacteria for approaching a realistic self-healing in concrete, Constr. Build. Mater. 68 (2014) 110–119.

[34] H. Huang, G. Ye, Z. Shui, Feasibility of self-healing in cementitious materials – By using capsules or a vascular system? Constr. Build. Mater. 63 (2014) 108–118.

[35] P. Minnebo, et al., A novel design of autonomously healed concrete: towards a vascular healing network, Materials 10 (1) (2017) 49.

[36] S. Joshi, et al., Microbial healing of cracks in concrete: a review, J. Ind. Microbiol. Biotechnol. 44 (11) (2017) 1511–1525.

[37] E. Ahn, et al., Principles and applications of ultrasonic-based nondestructive methods for self-healing in cementitious materials, Materials 10 (3) (2017) 278.

[38] N. De Belie, J. Wang, Bacteria-based repair and self-healing of concrete, J. Sustainable Cem. Based Mater. 5 (1–2) (2016) 35–56.

[39] K. Van Tittelboom, et al., Use of bacteria to repair cracks in concrete, Cem. Concr. Res. 40 (1) (2010) 157–166.

[40] V. Achal, A. Mukerjee, M. Sudhakara Reddy, Biogenic treatment improves the durability and remediates the cracks of concrete structures, Constr. Build. Mater. 48 (2013) 1–5.

[41] H. Mohammed, et al., The influence of incorporating plastic within concrete and the potential use of microwave curing. A review, J. Build. Eng. 32 (2020), 101824.

[42] S. Alnaimi, B. Elouadi, I. Kamal, Structural, Thermal and Morphology Characteristics of Low Density Polyethylene (2015).

[43] H. Layssi, et al., Electrical resistivity of concrete, Concr. Int. 37 (2015) 41.

[44] A.B. Jorge, R. Hazael, Use of Shewanella oneidensis for energy conversion in microbial fuel cells, Macromol. Chem. Phys. 217 (2016).

[45] BS 1881-113:2011, Testing concrete. Method for making and curing no-fines test cubes. 2011.

[46] Standard, B., Testing hardened concrete. Compressive Strength of Test Specimens, BS EN (2009) p. 12390-3.

[47] Standard, B., 12390-4. Testing Hardened Concrete. Compressive Strength. Specification for Testing Machines. British Standards Institution: London, UK, 2019.

[48] Standard, B., BS EN 1015-18: 2002. Methods of test for mortar for masonry. Determination of water absorption coefficient due to capillary action of hardened mortar. British Standards Institution, 2002.

[49] Standard, B., BS EN 1936:2006 Natural Stone Test Methods Determination of Real Density and Apparent Density, and of Total and Open Porosity. 2006.

[50] Nordest, N.B., Concrete mortar and cement-based repair materials: Chloride migration coefficient from non-steady-state migration experiments. 1999.

[51] Standard, B., EN 196-1. Methods of testing cement. Determination of strength. BSI 36 (2005). 2005.

[52] D.N. Saikia, J. Brito, Mechanical properties and abrasion behaviour of concrete containing shredded PET bottle waste as a partial substitution of natural aggregate, Constr. Build. Mater. 52 (2014) 236–244.

[53] S.-G. Choi, et al., Review on geotechnical engineering properties of sands treated by microbially induced calcium carbonate precipitation (MICP) and biopolymers, Constr. Build. Mater. 246 (2020), 118415.

[54] A. Van Wylick, et al., A review on the potential of filamentous fungi for microbial self-healing of concrete, Fungal Biol. Biotechnol. 8 (1) (2021) 16.

[55] F. Liendo, et al., Factors controlling and influencing polymorphism, morphology and size of calcium carbonate synthesized through the carbonation route: A review, Powder Technol. 398 (2022), 117050.

[56] H. Choi, et al., Control of the polymorphism of calcium carbonate produced by self-healing in the cracked part of cementitious materials, Appl. Sci. 7 (6) (2017) 546.