Chapter

Exploits, Advances and Challenges in Characterizing Self-Healing Materials

Camillus Sunday Obayi and Paul Sunday Nnamchi

Abstract

Characterization is an indispensable tool for understanding the structure–property-processing relationship in all material classes. However, challenges in self-healing materials characterization arise from the preparation routes, material types, damage mechanism and applications. Here, the discourse surveys the exploits, advances and challenges encountered within various characterization methods that have been exploited to reveal the damage-restoring processes in some material classes, namely metals, polymers, ceramics, concretes and coatings. Since there is no unified characterization procedure for the different classes of materials displaying self-repairing capabilities, the outcome of this discourse contributes to the advancement of knowledge about understanding self-healing testing procedures. An overview of methods, challenges and prospects toward self-healing property standardization at different length scales has been discussed.

Keywords: material characterization, properties, processing, challenges, test standardization, self-healing materials

1. Introduction

Characterization is a vital tool in elucidating the characteristics of material systems and ascertaining their suitability for various applications. Characterization is also an indispensable technique for quantifying self-repairing capabilities of various material classes. A self-healing material is a material designed to mimic nature, self-repair and restore its partial or original characteristics, thereby prolonging its service life like a biological system after encountering some form of damage induced by its service environment [1, 2].

Developing a man-made material capable of sensing and self-repairing in response to changes in the operating environment is a challenging task. This is because it takes a great exploit to design and process a synthetic material to mimic very closely the nature-designed mechanism of self-repair obtained in complex biological architectures. Numerous design approaches and preparatory routes have been attempted by research community to create self-healing abilities in different material classes for many applications. The material classes exploited so far include polymers, metals, ceramics, cements, coatings and composites [3].

Another huge task is quantifying the material's capability to self-repair and its suitability for a specific application via characterization techniques.

Several techniques have been employed to evaluate and quantify self-healing capacities and effectiveness in each of above material classes. Nevertheless, challenges arise in the characterization of self-healing materials as evaluation methods are not only materials and application specific, but also depend on the mechanism of the self-healing process. More so, self-healing processes take place on a very small length scale requiring sophisticated experimental procedures and equipment to unravel the mechanism of self-healing. Furthermore, it is important to establish a uniform testing procedure and standard for different material groups for better understanding of the concept [4]. This chapter surveys the main techniques applied to reveal the damage-restoring mechanisms in some material classes, but begins with a brief survey of preparatory routes and mechanisms of self-repair in the different materials classes.

2. Self-healing materials

Self-healing is the capability of a material to recover from any kind of damage automatically without any external intervention as obtainable in biological systems or with external stimulation such as heat, light, electrical stimulus and solvent. The materials that exhibit self-healing without any external intervention or stimuli are said to be autonomic while self-healing that involves human or external influence to induce healing is said to be nonautonomic in nature [5, 6]. One of the major problems encountered in the use of materials in diverse fields is how to ensure their durability and minimize structural failures [7]. A self-healing material is therefore an artificial material designed with built-in ability to detect failure and respond automatically to restore partial or full properties or function of the structure after encountering in-service damage [3, 7].

This in-service damage, which is usually in form of micro-scratches, surface and internal cracks, voids or other defects [8, 9], is majorly responsible for failure in materials systems. Over time, these micro-cracks accumulate and grow until catastrophic failure of the entire product or system occurs. Since this source of failure normally initiates at the nanoscale level and progresses subsequently to the micro- and macroscale levels until failure occurs, an ideal self-healing material would without any external influence prevent initiation of failure at these small length scales or repair already nucleated damage, thereby restoring the original material properties in a shortest time [3, 7]. Since the greater of the in-service damage encountered in material systems is usually in form of micro-cracks, voids or other defects, the objective of designing self-healing materials is to impart them with the capabilities to prevent the initiation of micro-cracks and voids or fill and seal them automatically.

For so many years now, the strategies of fabricating synthetic materials with the capability to self-heal like a biological system or as envisaged above have been exploited greatly. This huge interest is anchored on benefits of self-healing in materials. These benefits include enhancing materials' service lifetime, reduction in replacement costs and improvement in product safety [7]. Great advances have been witnessed in creation of self-healing materials since the birth of the concept. The concept has been exploited in almost all materials classes including polymers, metals, ceramics, cements, coatings and composites [3]. The design strategies and processing routes involved in creating self-healing capabilities in these material classes are different, just like their self-healing reactions to damage encountered during their lifetimes. The next subsection takes a look at the creation of self-healing abilities in these systems, the prevalent mode of failures and mechanisms of self-repairing.

3. Preparatory routes and mechanisms of self-healing

3.1 Self-healing polymers and polymer matrix composites

The self-healing concept has been most successful in the development of self-healing polymer-based systems [10, 11]. This emanates from the fast diffusion rate and high plasticity due to open-molecular structures in polymers, which facilitate diffusion of healing agents to fill and seal voids or micro-cracks [10] even at room temperature. Unlike metallic and ceramic systems, polymeric systems are light weight, chemically stable and can be easily processed [4]. These properties are exploited in developing efficient self-repairing polymers and polymer-based fiber-reinforced composites, which have applications in transportation, electronics, defense, biomedicine and construction industries [7, 12, 13].

Based on the strategies exploited to achieve self-repair, polymers are generally grouped into extrinsic and intrinsic self-healing systems [14]. Intrinsic self-repair is achieved by synthesis of smart polymers containing functional groups with the inherent ability to reversibly polymerize or cross-link their bonds in the presence of a stimulus like light or heat [15] and by so doing act as healing agents. The processes for obtaining extrinsic self-healing include (a) embedding microcapsules containing curable healing agents into polymer networks; and (b) incorporation of healing agents into polymer networks via microvascular channels [5, 16].

The microcapsule in (a) could be in form of capsule containing healing agent and catalyst or twin microcapsules each containing a monomer/resin and its hardener [5, 16, 17] while that in (b) can be in form of fibrous composite architecture impregnated with a microvessel filled with reactive healants [18]. Unlike extrinsic routes where healing agents are consumed during the curing process and are not replenished, intrinsic approaches have the advantage of multiple healing of damage in the same area owing to reversible polymerization [19]. Self-healing has been exploited and accomplished in thermoplastic, thermosetting and elastomeric systems.

The mode of damage often encountered in polymers and structural composites is in form of matrix micro-cracking, fiber breakage or delamination and fiber-matrix debonding [7, 20, 21]. Self-healing mechanism or recovery or recuperation takes place when a damage/crack is encountered and is healed by intrinsic polymerization or polymerization of healing agent as crack ruptures the capsules as in (a) or by favorable reaction kinetics and post-polymerization as in (b).

3.2 Self-healing metals

When compared to other material systems, it is much difficult to achieve self-healing in metals [22–24]. This is as a result of their high melting temperatures and strong atomic bonds, which limit diffusion of healing agents/solute atoms to sites of damage at low temperatures [22, 23]. There is also further restriction due to the relative small size and volume of the solute atoms. As a result, rate of mass transport to fill damage sites is intrinsically low at the usual low operating temperatures [23, 25].

The major factor limiting the useful life of metals is the occurrence of internal damage such as voids and cracks during processing or service. These defects usually initiate as nano- or micro-cracks in the bulk or on the surface, grow and propagate and eventually lead to failure. The self-healing process in metals in response to crack initiation follows the sequence of diffusion or release or transport of healing agents or atoms into the void or crack to fill and seal it, thereby restoring partially or fully the mechanical properties such as fatigue strength, stiffness and fracture toughness.

The approaches that have been proposed and attempted in developing self-healing in metallic systems according to [22] include: (a) precipitation-induced self-healing approach at low and high temperatures [26]; (b) dispersion of nano-shaped memory alloy (SMA) in off-eutectic metal matrix [27–29]; (c) SMA-clamp and melt [30]; (d) solder tubes/capsules; (e) coating agent [31] and (f) electro-healing [32, 33]. Blazej Grabowski and C. Cem Tasan [22] classified these concepts into two based on the healing length scale as (i) healing of nanoscale voids (which includes approaches a and b) and (ii) healing of macroscale cracks (which includes approaches c, d, e and f) [22]. One (I) and two (II) above were earlier classified into damage prevention and damage management by Van der Zwag et al. [34], respectively. This implies that healing at nanoscale targets prevention of macroscale damage while healing at macroscale focuses on management of macroscale damage to prevent total failure. Manuel [30] further classified approaches a and b as solid-state healing; approaches c, d and e as liquid-state healing and approach f as electrolyte-assisted healing. The self-healing concepts in metals and metal matrices are summarized in **Figure 1** and details of the features of these concepts are available in Ref. [22].

3.3 Self-healing ceramics

Ceramics are very important engineering material and are widely applied in electrical, magnetic, chemical, nuclear and biomedical fields [35]. However, ceramics have major shortcomings of being inherently porous and brittle in nature. As a result, ceramics have low strengths and fracture toughness as the components are prone to catastrophic failure by crack damage even at subcritical loading [36, 37]. Thus, self-healing concept in ceramics targets induced healing of structural defects (cracks and pores) in order to prolong lifetime [38].

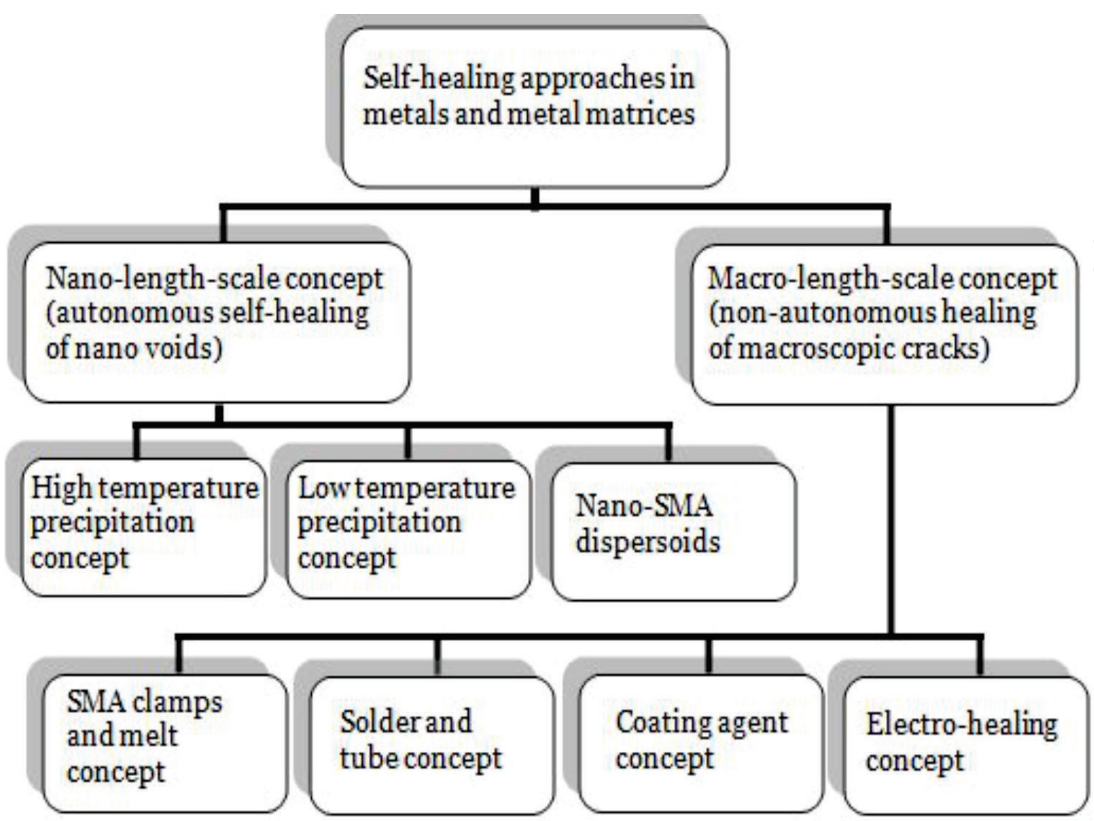

Figure 1.
Self-healing concepts in metals and metal matrices adapted from Ref. [22].

Self-healing in brittle ceramics has also witnessed extensive studies like polymers, but healing in ceramics is difficult to achieve at temperatures below 1000°C [35]. This is because self-repairing in ceramics takes place readily via solid-state diffusion, which requires high activation energy. This thermally activated solid-state reaction has the disadvantage of inhibiting long-range transport of material required to heal macro-cracks. More so, the healing of nano-cracks is inhibited by crack surface relaxation phenomena triggered by the ionic and covalent bonding character in ceramics [39]. Although, processing of self-healing ceramic materials is regarded as a high-temperature healing process, processing at lower temperatures is being pursued.

Some healing routes have been adopted to repair crack damages in ceramics at elevated temperatures. The important ones include crack closure enabled by diffusion-controlled sintering; crack opening rebonding promoted by viscous flow of glass phase; filling the crack opening space with products of oxidation reaction as obtainable in silicon carbide composites [35, 40] and healing of multicomponent and multiphase ceramic materials through local particle rearrangement-induced eutectic melt or phase transition [41]. Damage mechanisms and crack healing have been widely studied in various ceramic materials including single crystalline, polycrystalline and amorphous glasses.

3.4 Self-healing concrete materials

Concrete is the most popular cement-based material and most widely used constructional material [42, 43]. Concrete is regarded as a composite material made up of water (H_2O), cement, fine and coarse aggregates. It has many good qualities such as availability and affordability of its constituent materials, versatility, durability and low maintenance [42–45]. Concrete exhibits superior compressive strength, but low tensile strength. In order to improve its tensile strength, it is reinforced with steel bars [43]. However, the major limitation of concrete is its high susceptibility to cracking [43, 44]. The causes of cracks at both micro- and macro levels include preparation processes, temperature differences, shrinkage, fatigue loads and settlement of structures [42, 44]. The cracks serve as channels for water, dissolved particles in fluids and unwanted acidic gasses to penetrate the concrete [42, 45], attacking the concrete and corroding the steel reinforcement [44, 45]. Thus, the susceptibility of concrete to crack leading to structural failures is a major concern and has remained unsolved in industry [43].

However, concrete has been known to exhibit natural or autonomous self-healing to a certain extent under a long-term hydration [45]. It has been proved that some initial cracks in concrete can be suddenly closed when un-hydrated cement reacts with carbon dioxide dissolved in water, producing calcium carbonate, $CaCO_3$ [46, 47]. Thus, self-healing in cementitious materials can be obtained naturally or artificially [42]. The blocking of cracks through natural routes occurs owing to the following: expansion of hydrated cementitious matrix; precipitation of $CaCO_3$; presence of impurities in H_2O and further hydration of unreacted cement [42].

The artificial approach toward the development of self-healing cementitious materials targets enhancing the natural abilities of cement-based materials by engineering artificial healing abilities [42]. The artificial route focuses on filling of cracks by use of microorganism, polymers and addition of supplementary cementing materials to the concrete mix or steel fibers [45]. Microorganisms are biological agents and they are added in cement directly or in encapsulated forms to promote the precipitation of sealing compound such as $CaCO_3$ in a crack opening [48, 49]. Crack closure can also be achieved by addition of extra cement or other additives like fly ash to initial mix design to promote continuing hydration or stimulate a reaction process releasing self-sealing products [50, 51]. Self-healing in cementitious materials has also been attempted by incorporating polymers containing healing agents and shape memory materials into cement matrices [52, 53].

3.5 Self-healing coatings

Coatings can be defined as any thin layer of covering applied to the surface of a material. The basic objective of traditional coating is to separate material surfaces, especially metal surfaces from environmental corrosive attack. Most metallic materials have the intrinsic weakness of being corrodible in aqueous service environments. Corrosion normally starts at the surface and is adjudged one of the major causes of material failures. Coating acts as a barrier, limiting the diffusion of oxidation species such as oxygen and moisture to the metal surface [54]. For effective protection, the coating must maintain its adherence, structural integrity and not break down in the presence of operating factors such as mechanical stresses, abrasions, changes in pH, surface tension and temperature [54, 55].

However, over time, these operating factors lead to formation of scratches, surface and internal micro-cracks or even delamination, requiring human intervention to prevent or stop the interaction of the coated material surface and the unfriendly environment [55, 56]. The development of self-healing/smart coatings is driven by the need for damaged protective coatings to automatically sense or respond to damages and repair without human intervention when in service. Besides corrosion sensing, smart coatings have been applied to achieve self-cleaning and antifouling functions [54]. Intrinsic and extrinsic strategies have been adopted to impart self-healing capabilities in coatings using different materials of both organic and inorganic origins [54, 56], such as polymeric compounds [57], metals [58], ceramics [59] and composites [60].

Intrinsic self-healing coating can be obtained by using organic materials that undergo reversible chemistry [56] or self-reactions [61]. Extrinsic self-repair in organic coatings can be achieved by embedding self-healing agents or corrosion inhibitors in the structure of a polymer coating. The two popular methods of doing this are encapsulating healing agent in microcapsules (microencapsulation) or storing healing agents in capillary tubes (vascular networks) [55, 62]. Healing takes place when microcapsules or capillary tubes containing the healing/anticorrosion agents are ruptured by damage and release their contents, which flow into and heal the damaged areas [55, 62, 63]. The process of healing can come in form of blocking the active sites on the exposed metal surface after encountering damage. Besides storing healing agents in open polymer structures, nano-sized containers based on inorganic systems such silica, ceramic and TiO_2 have been reported to have high storing and release abilities [64–67].

In order to overcome the limitation of low storage capacity in microencapsulation-based polymeric and inorganic self-healing systems, nano-sized core-shell and microfiber containers are being exploited [68]. The major limitation of polymeric and inorganic containers is low storage capacity, depletion and noncontinuous replenishment of the healing agent contained within it on rupturing of a microcapsule. Currently, these concepts are being extended to layer-by-layer deposition, multi-shell-core microcapsules that can contain artificial or green anticorrosive agents that enable two-in-one action of self-healing and anticorrosion [69].

4. Characterization of self-healing materials

It has been obvious from past reviews on different materials systems that the major source of failures in materials is the presence of faults/damage such as voids, cracks or other defects introduced in the materials during processing or developed during utilization. Damage initiation usually starts with one or more cracks at microscopic level [70], which gradually propagate and grow in size and eventually lead to unexpected failure of the material [70, 71]. Hence, damage can be regarded as an accumulation of micro-damages that ultimately lead to material rupture if it is not repaired in due time [71]. Great efforts are spent in designing, processing and characterization to prevent the development of the damage or manage it using different self-healing strategies enabling longer service lives, greater safety and reduced maintenance costs.

For the above, self-repairing strategies target preventing, curing, by closing or filling or sealing of these cracks or voids on the surface or in the bulk of the materials by exploiting different self-healing approaches, whereas characterization focuses on proving that self-healing has taken place by determining the extent of recovery or restoration of initial properties after encountering damage(s). Much earlier than now, the characterization of self-healing capabilities in material systems concentrated mainly on the well-known macroscale evaluation, neglecting micro- and nanoscale events, responsible for initiation of material failure [71].

On the other hand, macroscale evaluation is not always sufficient, because it cannot provide comprehensive information about self-healing at all length scales or levels as it is focused mainly on the restoration of observable properties after the damage has occurred. However, it has the advantage of easier standardization when compared to microscale methods [72] as it is observable and the procedures most times are well known. To obtain a quantitative assessment and better understanding of the materials' self-healing abilities, there is need to complement macroscopic investigation with microscopic and nanoscale measurements [4, 6, 42] as self-healing processes take place on various length scales that might require sophisticated experimental procedures and equipment to reveal the mechanism of self-healing operation.

The quantification formula for estimating the capability of a given material to self-repair is the self-healing efficiency η, defined as the ability of a given material to recover a particular property relative to the virgin or undamaged material [73]. This formula, which was initially applied to polymeric materials [74], is now commonly adopted for comparing healing efficiencies in many material classes subjected to macroscopic quasi-static and dynamic tests. The expression for healing efficiency is shown in Eq. (1).

$$\eta = \frac{f_{healed}}{f_{virgin}} \text{X } 100\% \tag{1}$$

where f is a certain property of a particular material such as tensile strength, fracture toughness, tear strength, fatigue strength, flexural strength, creep rupture strength etc.

However, unlike other testing methods, monitoring or testing of self-healing materials in most cases entails inducing controlled damage such as a crack in the material and allowing it to heal using a particular healing treatment. This is followed by testing both the healed and virgin materials to failure. The extent of recovery of properties of the healed material is compared to original or virgin material properties using Eq. (1). The sequence of characterization is shown in **Figure 2a**.

Numerous quantification methods have been used for the assessment of self-healing capabilities for the different material systems. The characterization method adopted to quantify self-healing effectiveness should take into consideration the

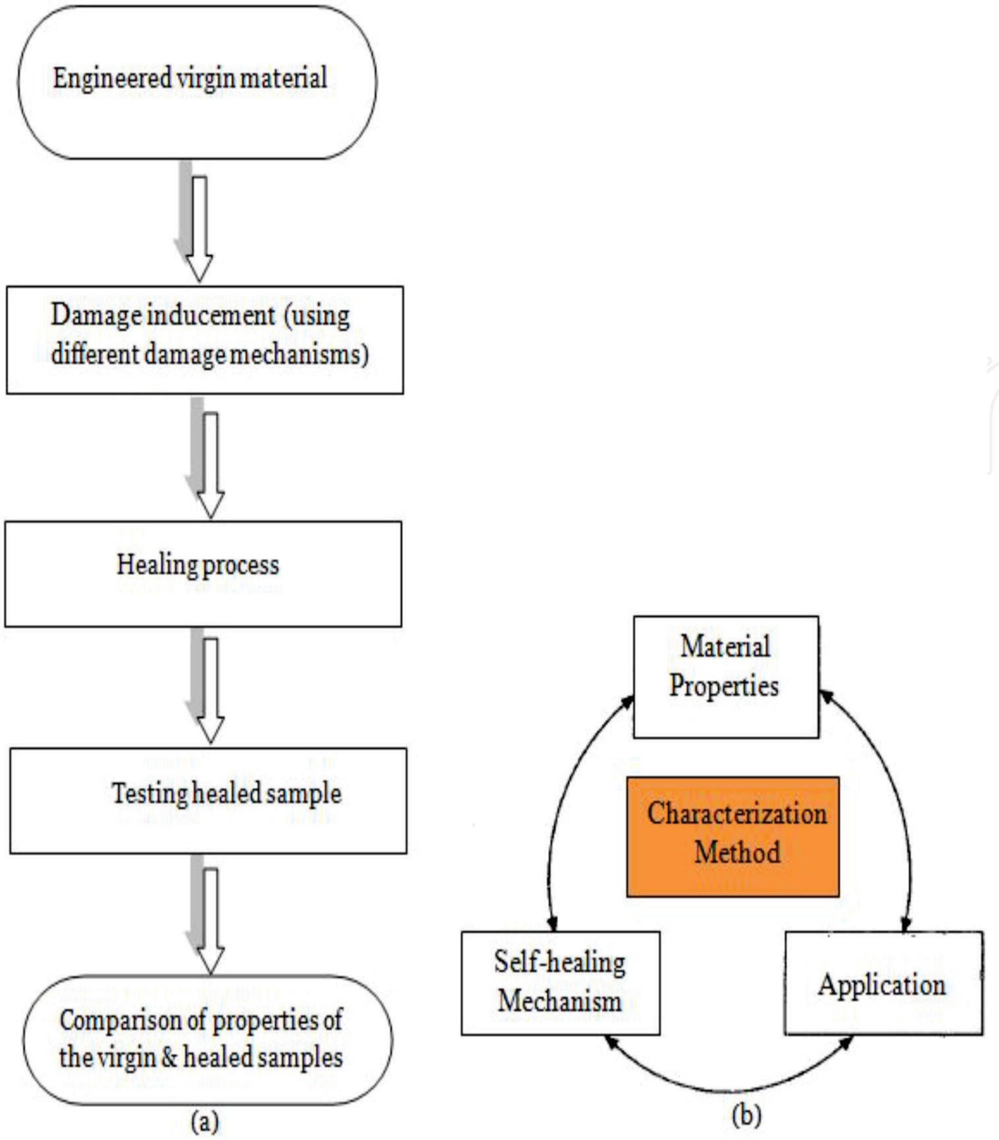

Figure 2.
(a) Steps in characterization of self-healing materials, and (b) interrelationship among material properties, self-healing mechanism, characterization method and application adapted from Ref. [6].

material properties developed, repairing mechanism and its intended application as shown in **Figure 2b** adapted from Ref. [6]. This subchapter considers quantification of healing efficiencies at different length scales in the above material classes.

4.1 General self-healing characterization techniques

4.1.1 Characterization of self-healing polymers and polymer matrix composites

Over the last few years, several testing methods have been used to assess self-repairing in polymers (thermosets, thermoplastics and elastomers) and polymer-based fiber-reinforced composites before and after repairing at macro-, micro- and nano/molecular levels. Even computational and/or predictive approaches have been attempted for deeper understanding of self-healing processes in polymer systems.

Macroscale healing evaluation leverages on fracture mechanics test procedures. Evaluation of healing requires inflicting some form of controlled crack/damage that resembles the mode of damage during utilization on the virgin polymer [73, 75, 76] by application of mechanical loads. This is accompanied by applying similar mechanical load of damage to the healed polymer and evaluation of recovery of the polymer from the fracture.

Depending on the mode of fracture, fracture evaluation loads could be in form of impact, fatigue, quasi-static fracture, tensile, compressive and flexural loads for mode I (opening) or mode III (tearing) fracture processes [71]. Also based on the type of polymeric system and the type of crack it develops under stress, the test samples have special geometries such as tapered double cantilever beam (TDCB); compact tension (CT) test specimens and width-tapered double-cantilever beam (WTDCB); double-cleavage drilled compression (DCDC); double-cantilever beam (DCB) and others [71]. These geometries and their suitability for evaluating the mechanical healing efficiencies in different polymers and polymer matrix composites are described in detail in Ref. [71].

The extent of recovery of various material properties (healing efficiency) is estimated using various forms of Eq. (1) after subjecting the damaged and undamaged samples to any or combination of the above mechanical loads as shown in Eqs. (2)–(6). The recovery of fracture toughness, flexural, tensile, impact and tear strengths has been quantified in different polymer healing systems with healing efficiencies ranging from 23 to 100% [7].

For instance, crack healing efficiency (η) for mode I type of healing can be estimated using Eq. (2) [7, 77].

$$\eta = \frac{K_{IC}^{healed}}{K_{IC}^{virgin}} X100\% \tag{2}$$

where K_{IC}^{healed} is the fracture toughness of a healed fracture specimen and K_{IC}^{virgin} is the fracture toughness of the virgin specimen.

An alternative expression for healing efficiency based on fracture energy [74, 77] is

$$\eta = \frac{G_{IC}^{healed}}{G_{IC}^{healed}} X100\% \tag{3}$$

where G_{IC}^{healed} and G_{IC}^{virgin} are the critical energy release rate from testing the healed fracture and virgin specimens, respectively.

Crack healing efficiency has also been defined in terms of fatigue life-extension [77, 78] as

$$\eta_d = \frac{N_{healed - N_{control}}}{N_{control}} \tag{4}$$

where N_{healed} and $N_{control}$ are the total number of cycles to failure for a self-healing sample and *for* similar sample without healing, respectively.

For elastomeric self-healing materials, the recovery of tear strength is used to define healing efficiency as

$$\eta = \frac{T_{healed}}{T_{virgin}} X100\% \tag{5}$$

where T_{healed} is the tear strength of the healed material and T_{virgin} is tear strength of virgin material.

Healing efficiency has also been estimated based on change in stiffness and recovery in a damaged and healed polymer [79] as

$$\eta = \frac{E_{healed}}{E_{virgin}} X100\% \tag{6}$$

Besides the macroscale methods used for mechanical performance evaluation of self-healing materials, evaluation at smaller length scale (micro- and nanoscale levels) is necessary to reveal the underlying healing mechanisms in polymers and deepen understanding of self-healing [6]. Characterization techniques at this scale enable the monitoring of the whole process of self-healing from stage of inflicting damage to identifying interactions and confirmation of healing functionality at molecular/nanolevels [16, 80]. The techniques include imaging, spectrometric, scattering, rheological and thermal techniques [6].

4.2 Characterization of self-healing metals

Self-healing efficiency quantification of metals based on the bulk material properties can also be carried out by subjecting pre-cracked samples to various mechanical tests and self-healing efficiency determined using Eq. (1). For instance, the self-healing efficiency of metallic system based on precipitation-induced approach can be evaluated by subjecting the age-hardened alloy (virgin alloy) and its pre-cracked counterpart but filled low-melting alloy to tensile loading to fracture. Alaneme and Omosule [81] used this method to determine the self-healing efficiency of underaged Al-Mg-Si alloys and 60Sn-40Pb alloy-reinforced aluminum metal–metal composites. The self-healing efficiency, η, was estimated using relation based on the tensile strength criterion given by Eq. (7):

$$\eta_{tensile} = \frac{\sigma_{healed}}{\sigma_{virgin}} X100\% \tag{7}$$

where σ_{virgin} is the tensile strength of the virgin specimen and σ_{healed} is the tensile strength of the healed specimen.

Other experimental techniques used to characterize solid materials subjected cyclic or creep loads can also be adapted to evaluate bulk metallic material systems.

Mechanical evaluation of materials using micro-indentation techniques is a widely accepted tool to reveal information on the surfaces of bulk hard materials [4] and it can be readily applied to study healing at micron scale. Self-mending at this length scale can be studied by inducing mechanical damage through micromachining accompanied by imaging of the repairing process. The imaging can be done using low and high imaging equipment such as optical microscope, scanning electron microscope (SEM), energy dispersive X-ray spectroscope (EDS) and environmental scanning electron microscope (ESEM) or X-ray micro-tomography instrument to provide details concerning crack propagation arrest [31] and evolution of self-healing reactions and to reveal evolved micro-structures and morphology [4]. The results obtained at micro- and nanolevels are used to buttress results at macrolevels.

Most research conducted on self-healing metals focused on either solid-state diffusion healing of micro-cracks, or shape memory alloy (SMA)-reinforced "off-eutectic" matrices. It is worthwhile to conduct tests at nanolevels to elucidate the bonding at the interface between the diffusing species and the metal matrices. Laha et al. [82] applied nanoscale investigation using Auger spectroscopy to show that boron (B) atom acts as a solute healing agent in 347-austenitic stainless steel by diffusing to the nano voids and precipitating at the void surfaces. He et al. [83] equally used positron annihilation spectroscopy to confirm that the addition of B and nitrogen (N) maximally accelerates the precipitation of copper (Cu) in iron-copper (Fe-Cu) alloy closing nano-voids in the system.

4.3 Characterization of self-healing ceramics

The current fracture mechanic tests used to assess self-healing capabilities in hard materials are also applicable to advanced ceramics, but the difficulty in creating controlled cracks in ceramic materials limits this application. Unlike other hard materials that exhibit some level of plasticity, ceramic materials are very brittle in nature and are prone to unwanted fast fracture under mechanical and thermal stresses [71]. Another limitation is that it is difficult achieve crack closure in ceramics at low temperatures. The most common procedure for creating controlled micro-cracks and quantifying healing efficiency is indentation method [84]. The healing efficiency is evaluated in terms of crack closure by comparing the control samples with the healed specimens.

For instance Nam and Hwang [40] investigated crack healing behavior of ZrO_2/SiC composite ceramics with TiO_2 additive. Cracks of about 100 μm were made on the sample surfaces using Vickers indenter. Since self-healing in ceramics is a high-temperature process, the indented samples were heat-treated to stimulate healing, but the test was conducted at room temperature. This was followed by observing the pre- and post-healed indents with X-ray diffractometer (XRD). The strength of crack closure was determined using three-point bending test. Li et al. [85] also used flexural test to evaluate the multiple healing of titanium aluminum carbide (Ti_2AlC) ceramic damaged by indentation in terms of crack propagation.

Besides using bending tests, tensile and the biaxial ball-on-three balls (B3B) tests have been used to study healing efficiencies in ceramics at room temperatures. Gao and Suo [86] assessed adhesion healing efficiency in a ceramic coating by performing tensile tests and correlating the healing time and residual stress while Harrer et al. [87] studied the healing of surface defects induced by different machining conditions on silicon nitride ceramic using biaxial ball-on-three balls.

All these tests are usually performed at room temperature while the healing process takes place at elevated temperatures >1000°C with the attendant oxidative atmosphere and thermal stresses. At high temperatures, the internal structure and mechanical performance of the ceramics could change due to the accompanying local melting and phase transformations [88]. Since mechanical performance under the above atmosphere will be different from that at low temperatures, there is the need to develop a more suitable method for the quantification of self-healing efficiency in ceramics [71] that takes into consideration the real service conditions. Attempts in this direction have been made by Ando et al. [89, 90], who determined *in situ* crack healing ability by conducting mechanical tests on some ceramics at elevated temperatures [89, 90].

4.4 Characterization of self-healing concrete

The major cause of mechanical failure in concrete is cracks. A crack not only lowers strength, but exposes the reinforcing steel components to corrosion. Self-healing targets crack closure or prevention of crack propagation to retain strength and reduce water permeability in order to maintain durability. Self-healing efficiency of concrete in hardened form has been determined by conducting tests at macro-, micro-, and nanoscale levels. Majority of the researchers evaluated the self-healing efficiency at macrostructural level, some at microscale level and very few authors at nanostructure level [42].

Just like other hard materials, quantification of healing efficiency on one hand relies on fracture mechanics tests, which involve creation of controlled cracks on concrete. The mechanical characterization procedure follows the sequence of controlled crack initiation in the matrix using the standard compression and bending tests, healing processing and retesting of the healed concrete using the same pre-cracking procedure [91]. The initiation of cracks without causing failure at certain level of stress and detection of crack development are very important in testing of concrete. To control crack initiation, some authors have applied a notch in the middle point of test sample [92] while some used three-point bending or four-point bending technique found to be more effective in crack initiation without causing failure [93–95].

Besides conducting compressive and flexural tests [45, 96, 97], the performance of concrete has also been assessed by other mechanical tests such as split tensile and toughness tests [98, 99] and stiffness tests [100]. Detection of crack initiation and its degree have been carried out using nondestructive complementary tests such as acoustic emission analysis [101], linear variable differential transformer [102] and ultrasonic pulse velocity [103, 104].

On the other hand, efficiency is also evaluated by conducting permeability tests on the pre-cracked concrete. Permeability test aims at determining how effective self-healing concrete can shield steel bars from corrosion [105]. Permeability tests are performed in simulated environments containing fluids such as chlorine or water under certain temperature [94, 105].

Microscale tests are employed to identify and characterize the deposited materials within cracks in the concrete after self-healing and are used to complement and reinforce reliability of macroscale tests [42]. These deposited materials are the calcium carbonate precipitation by different bacterial strains, hydration product as well as polymerized products. Several of these tests are conducted using the following sensitive equipment: scanning electron microscope (SEM), field emission scanning electron microscope (FESEM), and X-ray diffractometer (XRD). SEM is used to identify the morphology of the deposited materials within the cracks [106]. Self-healing performance is also assessed using Raman spectroscopy [16]. Furthermore, nanostructure test has been used to evaluate self-healing efficiency of concrete [107]. Tests conducted at nanoscale help in the determination of bonding strength at the interface between the deposited materials in the cracks and the concrete.

4.5 Characterization of self-healing coatings

The basic function of a traditional coating is to shield material surfaces, especially metal surfaces from fast corrosion in the environment. Smart coatings provide a spontaneous protection to metal surfaces upon chemical or mechanical damage [108]. This is achieved by release of inhibiting species in the coating architectures, which inhibits electrochemical interaction between the metal substrates and the environment [109]. The characterization techniques highlighted here are those traditionally used to study corrosion, but adapted for studying self-healing coatings on metals.

The testing techniques used to ascertain the self-healing properties of coatings have been generally grouped into two: electrochemical [55, 109, 110] and non-electrochemical techniques or physicochemical characterization as shown in **Figure 3** [55, 109]. Electrochemical techniques enable the quantification of self-healing efficiency by providing important information about kinetics of protection; formation of protective films and isolation of redox species [109]. The electrochemical techniques are further divided into conventional (global) electrochemical methods and localized electrochemical techniques [55, 109].

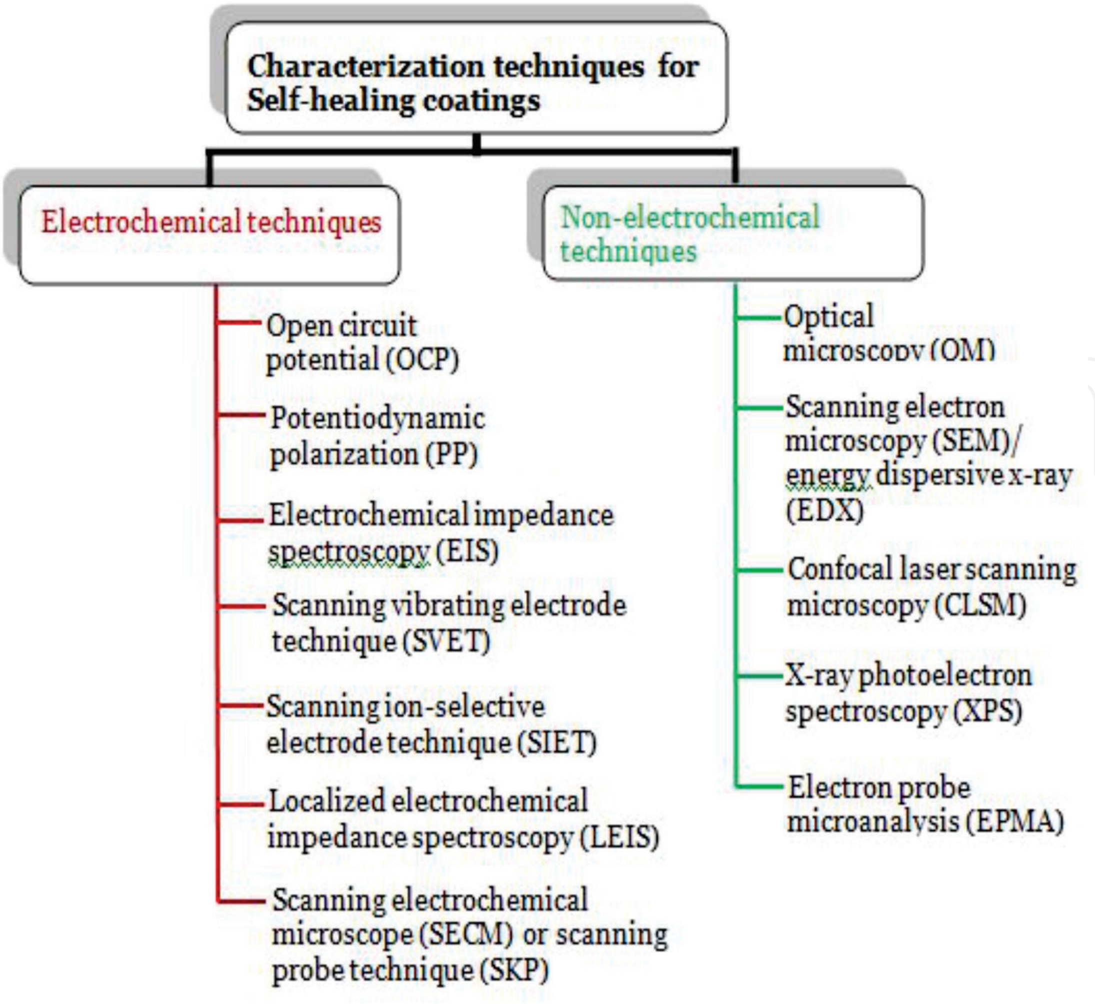

Figure 3.
Techniques for evaluating self-healing coatings adapted from [55].

The global electrochemical methods provide kinetic and deterministic information on self-healing processes, but they do not supply information about local reactions taking place at the site of damage. They include potentiodynamic polarization (PP), open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and they are the popular methods used for the study of corrosion and self-healing research [109]. For instance, PP and EIS give quantitative results about self-healing process enabling the determination of corrosion rate and protection efficiency [55]. Aramaki [111] employed the PP method to estimate the protection efficiency η_p of a protective polymer coating on an iron electrode surface using Eq. (8):

$$\eta_p = \frac{i^{\circ}_{corr} - i_{corr}}{i^{\circ}_{corr}} x100 \tag{8}$$

where i_{corr} is the corrosion current density with coating and i°_{corr} the is corrosion current density without coating.

Information about evolution of damage and healing of damage is provided by the local electrochemical methods, including micro-capillary cell, scanning vibrating electrode technique (SVET), scanning ion-selective electrode technique (SIET), scanning electrochemical microscope (SECM) or scanning probe technique (SKP) and localized electrochemical impedance spectroscopy (LEIS).

Each of these methods has advantages and limitations and should be used in combinations for detailed study of self-healing processes in coatings. Besides this, these electrochemical techniques should be complemented by conducting non-electrochemical or physicochemical analysis. Physicochemical analysis is majorly aimed at studying mechanism of self-healing coating protection—elemental analysis, interaction mechanisms between the metal substrate and the coating, morphology or phase transformation of the coating before and after healing. Surface analysis can be carried out with OM, SEM and CLSM, while energy dispersive X-ray (EDX), EPMA and XPS are useful for elemental analysis. The detailed description of the above test methods can be found in Refs. [55, 109, 112].

4.6 Challenges in the characterization of self-healing materials

Developing an artificial material to self-heal like a biological system comes as a huge task to the scientist or engineer. But more challenging is proving the material's self-healing capability and suitability for a particular application via characterization. Different approaches are used to achieve self-healing in different material classes based on their inherent properties. A self-healing material is an advanced material, a new product with new properties different from its original properties. It is important that the characteristics of the new product should be determined qualitatively or quantitatively. It is also important to monitor the changes during processing that led to the new properties. As a result, specific characterization methods are required to quantify self-healing efficiencies in each of the material classes. Most times, the equipment might not be common and sometimes unavailable unless improvised.

Unlike other characterization methods, evaluation of self-healing materials in most cases entails inducing a minimal expected mode of damage or failure during utilization on the material and using different methods to determine the extent of recovery/restoration of properties compared to original or virgin materials properties and to understand the mechanism of recovery. The methods of inducing the damage are different for the various material classes and even in the same material group. Inducing the appropriate damage simulating the real-life scenario is challenging. Also tasking is the selection of an appropriate testing procedure from an extensive range of known materials testing procedures that is adaptable and suitable for a particular self-healing concept. The field of self-healing materials is relatively new but a richly rewarding venture. The understanding of self-healing mechanisms in a variety of self-repairing material classes is still evolving. So also are the characterization methods needed to elucidate the dynamics of self-healing process. The challenges of harmonization of these methods in various research groups are yet to be resolved.

More so, the mode of damage is different and unique to the damaged material and its intended applications. Even within the same material class, there are various self-healing approaches and evaluation strategies. This makes the adopted routine of assessing the performance of the modified material and comparing its properties to the unmodified, virgin material complex. This makes it equally arduous to establish a common testing procedure for similar or for different materials classes.

5. Prospects for standardization of characterization techniques

Most of the current characterization methods used to quantify the healing performance focused on the macroscopic evaluation of recovery from macroscopically applied damage. However, early stage of damage and recovery occur at sub-macro level. Therefore, macroscopic evaluation cannot by itself be sufficient enough for self-healing quantification [4]. As the materials' failure normally starts at nano- and microscale levels, a sufficient and necessary quantification approach should take into consideration the damaging and healing events at these small length scales [71], more so, when they can easily be prevented or healed faster at the sublevels.

However, inflicting of macroscopic damage on hard self-healing materials, though far from the actual utilization conditions, can be easily replicated and holds the promise of easier standardization and comparison across similar materials [71]. Since damage initiation inherently starts at the microscopic/nanoscale level, inflicting of damage protocol can be done at microscopic level using nano- or/and micro-indentation techniques. Mechanical damage can be induced using micromachining, accompanied by imaging of the mending process using high-resolution imaging equipment such as environmental scanning electron microscope (ESEM) [4]. Currently, micro-indentation testing protocol is widely accepted and standardized tool for mechanical testing of materials [113]. *In situ* measurement techniques can also be very helpful in such environment, where dynamic and on process conditions can be captured or easily replicated. At the heart of this standardization prospect is the operator's skill.

Microscopic evaluation has limitations. One challenge is the requirement of very small volume of samples, which makes sampling difficult due to the nonhomogeneous composition of some materials [4]. Another is that it is not very suitable for testing soft materials. However, most of the self-healing material classes are hard materials. Some polymers, metals, ceramics, concrete and some coatings, especially inorganic coatings are all hard materials. Testing using micro-indentation technique complemented with macroscopic methods could be a useful step toward standardization of quantification in hard self-healing materials.

In practical situations, a single applied load affects more than one specific material's property and self-healing efficiency is regarded as the ability of a given material to recover a specific property relative to the virgin specimen. In this situation, efficiency calculation should take the combined properties of the material affected by the load into consideration and should be reported as an average or overall efficiency. The use of overall efficiency as a method of assessing performance of distinct materials using different test methods opens a path toward standardization irrespective of testing method and material class [71].

6. Future trends

The adopted routine of assessing the performance of self-healing materials has been to characterize the modified self-healing material and compare its properties to the unmodified, virgin material. An extensive literature survey indicated that it was difficult to find researchers who evaluated self-healing performance at macro-, micro- and nanostructural levels simultaneously. This is probably because the field is relatively new. Today, it is becoming obvious that an appropriate performance assessment method should take into account the damaging and healing at macroscopic as well as microscale/nanoscale levels. In order to achieve this, a combined suitable and reproducible evaluation procedure must be exploited for a better understanding of damage mechanism and healing process.

It is equally hard to find researchers who investigated several properties at the same time in one material. In real-life situations, the damage initiation and eventual failure can be caused by combined factors/loads-tensile, compressive, cyclic, bending, creep, thermal loads and others. The self-healing efficiency is defined as the ability of a given material to recover a specific property relative to the virgin or undamaged specimen [75]. For instance, a single applied load affects more than one specific material's property and efficiency calculation should take into account other properties of the materials affected by the load [71]. Therefore, the most appropriate evaluation approach should be the one that takes into account more than one property and reports combined efficiencies or overall efficiency, equal to prime average of the efficiency obtained for each material property [71].

A case could also be made to suggest or define effective predictive approaches or methods that would lead to faster evaluation and design of self-healing quantifications in materials at various length scales.

7. Concluding remarks

The development of self-healing materials comes as a huge challenge to the scientist or engineer—the challenge of synthesizing smart materials that can self-repair, elucidating the healing mechanism and proving their self-healing capabilities through characterization. There are many material classes and different approaches have been attempted to achieve self-healing capabilities in these materials. For close to two decades, several self-healing materials have been developed and many methods have been employed to assess self-healing behavior and determine healing efficiency of these materials. As the materials are different, so are the evaluation techniques utilized to characterize the healing behaviors. Besides taking into consideration the type of material, the healing-enabling preparatory route and repairing mechanism, the most suitable test method should fit the intended application. For completeness, effective characterization should be the one encompassing all length scales—macro-, micro- and nanoscale levels. Thus, an ideal quantification approach needs to take into account the macroscopic as well as microscale aspects of damaging and healing.

Among the several characterization methods utilized to investigate self-healing behavior and determine healing efficiency in metals, polymers and polymer composites, ceramics and concrete at macroscale evaluation focusing on restoration of mechano-physical properties is popular. Typically, most characterization methods in metals are carried out at the macroscale level, but healing takes place at nanoscale level. This can be a fundamental limitation in the characterization process for metals. However, evaluation techniques at micro- and nanoscale levels have been employed to link and correlate mechanical healing with underlying molecular processes in particular polymeric materials. However, testing of polymers and other material systems do come with their own challenges, including getting reliable information from testing of modified materials only with the available small-scale samples and at laboratory conditions. Long-time instability of polymers is also a problem as it has been demonstrated that the healing efficiency of extrinsic self-healing systems decreases over time.

In ceramics and concrete, initiation of controlled damage is somewhat tasking due to their inherent brittleness and low diffusion rate of healing agents. This is also likened to metals, whose self-healing mostly occurs faster at high temperature, but damage initiates at low temperature. Therefore, simulating the real condition of damage and healing simultaneously is a herculean task. On the other hand, coating is used in various conditions, but the nanoscale evaluation of indentation is carried out at controlled environments, which are different from its real application condition.

Conflict of interest

The authors declare no conflicts of interest with respect to the authorship and publication of this chapter.

Author details

Camillus Sunday Obayi* and Paul Sunday Nnamchi
Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka, Nigeria

*Address all correspondence to: camillus.obayi@unn.edu.ng

References

[1] der ZS V. Self-Healing Materials: An Alternative Approach to 20th Centuries of Materials Science. Berlin: Springer; 2007. pp. 161-193. DOI: 10.1515/ci.2008.30.6.20

[2] Hayes SA, Jones FR, Marhiya K, Zhang W. Self-healing composite materials. In: Proceedings of the 15th International Conference on Composite Materials. Durban; 27 June-1 July 2005. pp. 24-26

[3] Sitnikov NN, Khabibullina IA, Mashchenko VI, Rizakhanov RN. Prospects of application of self-healing materials and technologies based on them inorganic materials. Applied Research. 2018;**9**(5):785-793. DOI: 10.1134/S207511331805026X

[4] Lucas SS, Nellesen A, Von TM. Assessment of self-healing capabilities: A route towards standardization. In: Proceedings of the 4th International Conference on Self-Healing Materials (ICSHM2013); 17-19 June 2013. Ghent, Belgium: ICSHM; 2013

[5] Madara SR, Srath Raj NS, Selvan CP. Review of research and developments in self healing composite materials. IOP Conference Series: Materials Science and Engineering. 2018;**346**:012011. DOI: 10.1088/1757-899X/346/1/012011

[6] Bode S, Enke M, Hernandez M, Bose RK, Grande AM, Schubert US, et al. Characterization of self-healing polymers: From macroscopic healing tests to the molecular mechanism. Advances in Polymer Science. 2015;**273**:113-142. DOI: 10.1007/12_2015_341

[7] Aïssa B, Therriault D, Haddad E, Jamroz W. Self-healing materials systems: Overview of major approaches and recent developed technologies. Advances in Materials Science and Engineering. 2012:854203. DOI: 10.1155/2012/854203

[8] Pang JWC, Bond IP. Bleeding composites—Damage detection and self-repair using a biomimetic approach. Composites Part A: Applied Science and Manufacturing. 2005;**36**:183-188. DOI: 10.1016/j.compositesa.2004.06.016

[9] Jones S, Rule JD, Moore JS, Sottos NR, White SR. Life extension of self-healing polymers with rapidly growing fatigue cracks. Journal of the Royal Society, Interface. 2007;**4**:395-403. DOI: 10.1098/rsif.2006.0199

[10] Trask RS, Williams H, Bond IP. Self-healing polymer composites: Mimicking nature to enhance performance. Bioinspiration & Biomimetics. 2007;**2**:1-9. DOI: 10.1088/1748-3182/2/1/P01

[11] Sanada K, Yasuda I, Shindo Y. Transverse tensile strength of unidirectional fibre-reinforced polymers and self-healing of interfacial deboning. Plastics, Rubber and Composites. 2006;**35**:67-72. DOI: 10.1179/174328906X79914

[12] Wu DY, Meure S, Solomon D. Self-healing polymeric materials: A review of recent developments. Progress in Polymer Science. 2008;**33**:479-522. DOI: 10.1016/j.progpolymsci.2008.02.001

[13] Liu Y-L, Chuo T-W. Self-healing polymers based on thermally reversible Diels–Alder chemistry. Polymer Chemistry. 2013;**4**:2194-2205

[14] Kuhl N, Bode S, Hager MD, Schubert US. Self-healing polymers based on reversible covalent bonds. In: Hager MD, Zwaag VS, Schubert US, editors. Self-Healing Materials. Advanced Polymer Science. Switzerland: Springer International Publishing; 2016. pp. 1-58. DOI: 10.1007/12_2015_336

[15] Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR. Self-healing polymers and composites. Annual Review of Materials Research. 2010;**40**:179-211. DOI: 10.1146/annurev-matsci-070909-104532

[16] Bekas DG, Tsirka K, Baltzis D, Paipetis AS. Self-healing materials: A review of advances in materials, evaluation, characterization and monitoring techniques. Composites Part B Engineering. 2016;**87**:92-119. DOI: 10.1016/j.compositesb.2015.09.057

[17] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. Natural Product Letters. 2001;**409**:794-797. DOI: 10.1038/35057232

[18] Patrick JF, Hart KR, Krull BP, Diesendruck CE, Moore JS, White SR, et al. Continuous self-healing life cycle in vascularized structural composites. Advanced Materials. 2014;**26**(25):4302e8. DOI: 10.1002/adma.201400248

[19] Garcia SJ. Effect of polymer architecture on the intrinsic self-healing character of polymers. European Polymer Journal. 2014;**53**:118-125. DOI: 10.1016/j.eurpolymj.2014.01.026

[20] Mulville DR, Wolock I. Failure of polymer composites. In: Andrews EH, editor. Developments in Polymer Fracture. London: Applied Science Publishers; 1979. pp. 263-316

[21] Greenhalgh ES. Failure Analysis and Fractography of Polymer Composites. Cambridge: Woodhead Publishing Ltd; 2009. pp. 1-608

[22] Grabowski B, Tasan CC. Self-healing metals. In: Hager M, van der Zwaag S, Schubert U, editors. Self-Healing Materials. Advances in Polymer Science. Vol. 273. Cham: Springer; 2016. pp. 387-407. DOI: 10.1007/12_2015_337

[23] van Dijk N, van der Zwaag S. Self-healing phenomena in metals, special issue: Self-healing materials. Advanced Materials Interfaces. 2018;**5**:7. DOI: 10.1002/admi.201800226

[24] Ferguson JB, Schultz BF, Rohatgi PK. Self-healing metals and metal matrix composites. Journal of Metals. 2014;**66**(6):866-871. DOI: 10.1007/s11837-014-0912-4

[25] Zwaag SV. Routes and mechanisms towards self healing behaviour in engineering materials. Bulletin of the Polish Academy of Sciences: Technical Sciences. 2010;**58**(2):226-237. DOI: 10.2478/v10175-010-0022-6

[26] Alaneme KK, Bodunrin MO. Self-healing using metallic material systems-a review. Applied Materials Today. 2017;**6**:9-15. DOI: 10.1016/j.apmt.2016.11.002

[27] Rohatgi PK. Al-shape memory alloy self-healing metal matrix composite. Materials Science and Engineering A. 2014;**619**:73-76. DOI: 10.1016/j.msea.2014.09.050

[28] Baxevanis T, Parrinello AF, Lagoudas DC. On the fracture toughness enhancement due to stress-induced phase transformation in shape memory alloys. International Journal of Plasticity. 2013;**50**:158-169. DOI: 10.1016/j.ijplas.2013.04.007

[29] Grabowski B, Tasan C. Towards self-healing metals by employing optimally dispersed Ti-Ni shape memory nano-particles, project within DFG SPP 1568. In: Design and Generic Principles of Self-healing Materials. Bonn: DFG; 2014

[30] Manuel MV. Principles of self-healing in metals and alloys: An introduction. In: Ghosh G, editor. Self-Healing Materials: Fundamentals, Design Strategies, and Applications. Wiley-VCH; 2009. pp. 251-263

[31] Leser PE. Mitigation of Crack Damage in Metallic Materials, Report by National Aeronautics and Space Administration. NASA/TM–2014-218272. 2014. Available from: https://ntrs.nasa.gov/search.jsp?R=20140006911 2020-05-20T08:19:01+00:00Z

[32] Zheng XG, Shi YN, Lu K. Electro-healing cracks in nickel. Materials Science and Engineering A. 2013;**561**:52-59. DOI: 10.1016/j.msea.2012.10.080

[33] Zhou Y, Guo J, Gao M, He G. Crack healing in a steel by using electropulsing technique. Materials Letters. 2004;**58**(11):1732-1736. DOI: 10.1016/j.matlet.2003.10.049

[34] Zwaag VS. An introduction to material design principles: Damage prevention versus damage management. In: Zwaag VS, editor. Self Healing Materials. Vol. 100. Dordrecht: Springer Series in Materials Science, Springer; 2007. pp. 1-18. DOI: 10.1007/978-1-4020-6250-6_1

[35] Greil P. Generic principles of crack-healing ceramics. Journal of Advanced Ceramics. 2012;**1**(4):249-267. DOI: 10.1007/s40145-012-0020-2

[36] Ayatollahi MR, Aliha MRM. Fracture analysis of some ceramics under mixed mode loading. Journal of the American Ceramic Society. 2011;**94**(2):561-569. DOI: 10.1111/j.1551-2916.2010.04076.x

[37] Suresh S, Shih CF, Morrone A, O'Dowd NP. Mixed-mode fracture toughness of ceramic 1007 materials. Journal of the American Ceramic Society. 1990;**73**(5):1257-1267. DOI: 10.1111/j.1151-2916.1990.tb05189.x

[38] Houjou K, Ando K, Takahashi K. Crack-healing behaviour of ZrO_2/SiC composite ceramics. International Journal of Structural Integrity. 2010;**1**(1):73-84. DOI: 10.1108/17579861011023810

[39] Jarvis EA, Carter EA. A nanoscale mechanism of fatigue in ionic solids. Nano Letters. 2006;**6**(3):505-509. DOI: 10.1021/nl0525655

[40] Nam KW, Hwang JR. The crack healing behavior of ZrO_2/SiC composite ceramics with TiO_2 additive. Journal of Mechanical Science and Technology. 2012;**26**:2093-2096. DOI: 10.1007/s12206-012-0521-5

[41] Jun L, Zheng ZX, Ding HF, Jin ZH. Preliminary study of the crack healing and strength recovery of Al_2O_3-matrix composites. Fatigue and Fracture of Engineering Materials and Structures. 2004;**27**:89-97. DOI: 10.1111/j.1460-2695.2004.00725.x

[42] Muhammad NZ, Shafaghat A, Keyvanfar A, Abd. Majid MZ, Ghoshal SK, Yasouj SEM, et al. Tests and methods of evaluating the self-healing efficiency of concrete: A review. Construction and Building Materials. 2016;**112**:1123-1132. DOI: 10.1016/j.conbuildmat.2016.03.017

[43] Pour-Ghaz M, Weiss J. Detecting the time and location of cracks using electrically conductive surfaces. Cement and Concrete Composites. 2011;**33**:116-123. DOI: 10.1016/j.cemconcomp.2010.09.015

[44] Durga CSS, Ruben N. Assessment of various self healing materials to enhance the durability of concrete structures. Annales de Chimie–Science des Matériaux. 2019;**43**(2):75-79. DOI: 10.18280/acsm.430202

[45] Lucas SS, Moxham C, Tziviloglou E, Jonkers H. Study of self-healing properties in concrete with bacteria encapsulated in expanded clay. Science and Technology of Advanced Materials. 2018;**30**:93-98. DOI: 10.1016/j.stmat.2018.11.006

[46] Reinhardt H, Joos M. Permeability and self-healing of cracked concrete as a function of temperature and crack width. Cement and Concrete Research. 2003;**33**(7):981-985. DOI: 10.1016/S0008-8846(02)01099-2

[47] Hearn N. Self-sealing, autogenous healing and continued hydration: What is the difference? Materials and Structures. 1998;**31**:563-567. DOI: 10.1007/BF02481539

[48] Muynck WD, Debrouwer D, De Belie N, Verstraete W. Bacterial carbonate precipitation improves the durability of cementitious materials. Cement and Concrete Research. 2008;**38**:1005-1014. DOI: 10.1016/j.cemconres.2008.03.005

[49] Stuckrath C, Serpell R, Valenzuela LM, Lopez M. Quantification of chemical and biological calcium carbonate precipitation: Performance of self-healing in reinforced mortar containing chemical admixtures. Cement and Concrete Composites. 2014;**50**:10-15. DOI: 10.1016/j.cemconcomp.2014.02.005

[50] Termkhajornkit P, Nawa T, Yamashiro Y, Saito T. Self-healing ability of fly ash-cement systems. Cement and Concrete Composites. 2009;**31**:195-203. DOI: 10.1016/j.cemconcomp.2008.12.009

[51] Rahmani H, Bazrgar H. Effect of coarse cement particles on the self-healing of dense concretes. Magazine of Concrete Research. 2015;**67**:476-486. DOI: 10.1680/macr.14.00158

[52] Perez G, Gaitero JJ, Erkizia E, Jimenez I, Guerrero A. Characterization of cement pastes with innovative self-healing system based in epoxy-amine adhesive. Cement and Concrete Composites. 2015;**60**:55-64. DOI: 10.1016/j.cemconcomp.2015.03.010

[53] Wang X, Zhao J, Chen M, Ma L, Zhao X, Dang ZM, et al. Improved self-healing of polyethylene/carbon black nanocomposites by their shape memory effect. The Journal of Physical Chemistry. B. 2013;**117**:1467-1474. DOI: 10.1021/jp3098796

[54] Vijayan P, Al-Maadeed M. Self-repairing composites for corrosion protection: A review on recent strategies and evaluation methods. Materials. 2019;**12**(2754):1-17. DOI: 10.3390/ma12172754

[55] Fayyad EM, Almaadeed MA, Jones A, Abdullah M. Evaluation techniques for the corrosion resistance of self-healing coatings. International Journal of Electrochemical Science. 2014;**9**:4989-5011

[56] Shi X, Fernando BMD, Croll S. Concurrent physical aging and degradation of cross-linked coating systems in accelerated weathering. Journal of Coating Technology and Research. 2008;**5**:299-309. DOI: 10.1007/s11998-008-9081-0

[57] DaConceicao TF, Scharnagl N, Dietzel W, Hoeche D, Kainer KU. Study on the interface of PVDF coatings and HF-treated AZ31 magnesium alloy: Determination of interfacial interactions and reactions with self-healing properties. Corrosion Science. 2011;**53**:712-719. DOI: 10.1016/j.corsci.2010.11.001

[58] Koleva DA, Boshkov N, Bachvarov V, Zhann H, de Wit JHW, van Breugel K. Application of PEO_{113}–b-PS_{218} nano-aggregates for improved protective characteristics of composite zinc coatings in chloride-containing environment. Surface and Coating Technology. 2010;**204**(23):3760-3772. DOI: 10.1016/j.surfcoat.2010.04.043

[59] Gao J, Suo J. Modeling the barrier properties of polymer-layered silicate nanocomposites. Surface and Coating Technology. 2001;**34**(26):9189-9192. DOI: 10.1021/ma010780b

[60] Moustafa EM, Dietz A, Hochsattel T. Manufacturing of nickel/nanocontainer composite coatings. Surface and Coating Technology. 2013;**216**:93-99. DOI: 10.1016/j.surfcoat.2012.11.030

[61] Cordier P, Tournilhac F, Soulie-Ziakovic C, Leibler L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature. 2008;**451**:977-980. DOI: 10.1038/nature06669

[62] Zhu DY, Rong MZ, Zhang MQ. Self-healing polymeric materials based on microencapsulated healing agents: From design to preparation. Progress in Polymer Science. 2015;**49-50**:175-220. DOI: 10.1016/j.progpolymsci.2015.07.002

[63] Toohey KS, Sottos NR, Lewis JA, Moore JS, White SR. Self-healing materials with microvascular networks. Nature Materials. 2007;**6**:581-585. DOI: 10.1038/nmat1934

[64] Maia F, Tedim J, Lisenkov AD, Salak AN, Zheludkevich ML, Ferreira MGS. Silica nanocontainers for active corrosion protection. Nanoscale. 2012;**4**:1287-1298. DOI: 10.1039/C2NR11536K

[65] Kartsonakis IA, Balaskas AC, Koumoulos EP, Charitidis CA, Kordas GC. Incorporation of ceramic nanocontainers into epoxy coatings for the corrosion protection of hot dip galvanized steel. Corrosion Science. 2012;**57**:30-41. DOI: 10.1016/j.corsci.2011.12.037

[66] Arunchandran C, Ramya S, George RP, Mudali UK. Self-healing corrosion resistive coatings based on inhibitor loaded TiO2 nanocontainers. Journal of the Electrochemical Society. 2012;**159**:C552-C559. DOI: 10.1149/2.020212jes

[67] Lamaka SV, Zheludkevich ML, Yasakau KA, Serra R, Poznyak SK, Ferreira MGS. Nanoporous titania interlayer as reservoir of corrosion inhibitors for coatings with self-healing ability. Progress in Organic Coating. 2007;**58**(2-3):127-135. DOI: 10.1016/j.porgcoat.2006.08.029

[68] Zheng Z, Schenderlein M, Huang X, Brownbill NJ, Blanc F, Shchukin D. Influence of functionalization of nanocontainers on self-healing anticorrosive coatings. ACS Applied Materials & Interfaces. 2015;**7**:22756-22766. DOI: 10.1021/acsami.5b08028

[69] Jadhav RS, Mane V, Bagle AV, Hundiwale DG, Mahulikar PP, Waghoo G. Synthesis of multicore phenol formaldehyde microcapsules and their application in polyurethane paint formulation for self-healing anticorrosive coating. International Journal of Industrial Chemistry. 2013;**4**:31. DOI: 10.1186/2228-5547-4-31

[70] Darabi MK, Abu Al-Rub RK, Little DN. A continuum damage mechanics framework for modeling microdamage healing. International Journal of Solids and Structures. 2012;**49**(3-4):492-513. DOI: 10.1016/j.ijsolstr.2011.10.017

[71] Lucas SS, Tapavicza MV, Schmid AM, Bertling J, Nellesen A. Study of quantification methods in self-healing ceramics, polymers and concrete: A route towards standardization. Journal of Intelligent Material Systems and Structures. 2016:1-22. DOI: 10.1177/1045389X16641205

[72] Zhu HH, Zhou S, Yan ZG, JU JW, Chen Q. A two-dimensional micromechanical damage-healing model on micro-crack induced damage for microcapsule-enabled self-healing cementitious composites under tensile loading. International Journal of Damage Mechanics. 2015;**24**(1):95-115. DOI: 10.1177%2F1056789514522503

[73] Mauldin TC, Kessler MR. Self-healing polymers and composites.

International Materials Review. 2010;**55**(6):317-346. DOI: 10.1179/095066010X12646898728408

[74] Wool RP, O'Connor KM. A theory of crack healing in polymers. Journal of Applied Physics. 1981;**52**(10):5953-5963. DOI: 10.1063/1.328526

[75] Williams G, Trask RS, Bond IP. A self-healing carbon fibre reinforced polymer for aerospace applications. Composites Part A: Applied Science and Manufacturing. 2007;**38**(6):1525-1532. DOI: 10.1016/j.compositesa.2007.01.013

[76] Blaiszik BJ, Sottos NR, White SR. Nanocapsules for self-healing materials. Composites Science and Technology. 2008;**68**:978-986. DOI: 10.1016/j.compscitech.2007.07.021

[77] Kessler MR. Self-healing: A new paradigm in materials design. Proceedings of the Institution of Mechanical Engineers, Part G. 2007;**221**:479-495. DOI: 10.1243%2F09544100JAERO172

[78] Brown EN, Sottos NR, White SR. Fracture testing of a self-healing polymer composite. Experimental Mechanics. 2002;**42**(4):372-379. DOI: 10.1007/BF02412141

[79] Zako M, Takano N. Intelligent material systems using epoxy particles to repair microcracks and delamination damage in GFRP. Journal of Intelligent Material Systems and Structures. 1999;**10**:836-841. DOI: 10.1106%2FYEIH-QUDH-FC7W-4QFM

[80] Yin T, Rong MZ, Zhang MQ, Yang GC. Self-healing epoxy composites - Preparation and effect of the healant consisting of microencapsulated epoxy and latent curing agent. Composites Science and Technology. 2007;**67**:201-212. DOI: 10.1016/j.compscitech.2006.07.028

[81] Alaneme KK, Omosule OI. Experimental studies of self healing behaviour of under-aged Al-Mg-Si alloys and 60Sn-40Pb alloy reinforced aluminium metal-metal composites. Journal of Minerals and Materials Characterization and Engineering. 2015;**3**:1-8. DOI: journal/PaperInformation.aspx?PaperID=52698&#abstract

[82] Laha K, Kyono J, Kishimoto S, Shinya N. Beneficial effect of B segregation on creep cavitation in a type 347 austenitic stainless steel. Scripta Materialia. 2005;**52**(7):675-678. DOI: 10.1016/j.scriptamat.2004.11.016

[83] He SM, van Dijk NH, Schut H, Peekstok ER, Zwaag SV. Thermally activated precipitation at deformation-induced defects in Fe-Cu and Fe-Cu-B-N alloys studied by positron annihilation spectroscopy. Physical Review B. 2010;**81**:094103. DOI: 10.1103/PhysRevB.81.094103

[84] Le BE. Contact response of ceramics. Comptes Rendus Mécanique. 2011;**339**(7-8):466-472. DOI: 10.1016/j.crme.2011.05.005

[85] Li S, Song G, Kwakernaak K, Der Zwaag S, Slot GW. Multiple crack healing of a Ti2AlC ceramic. Journal of the European Ceramic Society. 2012;**32**(8):1813-1820. DOI: 10.1016/j.jeurceramsoc.2012.01.017

[86] Gao J, Suo J. Effects of heating temperature and duration on the microstructure and properties of the self healing coatings. Surface and Coatings Technology. 2011;**206**(6):1342-1350. DOI: 10.1016/j.surfcoat.2011.08.059

[87] Harrer W, Danzer R, Morrell R. Influence of surface defects on the biaxial strength of a silicon nitride ceramic – Increase of strength by crack healing. Journal of the European Ceramic Society. 2012;**32**(1):27-35. DOI: 10.1016/j.jeurceramsoc.2011.07.019

[88] Yang HJ, Pei YT, Rao JC, De Hosson TM, Li SB, Song GM. High temperature healing of Ti2AlC: On the origin of inhomogeneous oxide scale. Scripta Materialia. 2011;**65**(2):135-138. DOI: 10.1016/j.scriptamat.2011.03.031

[89] Ando K, Shirai Y, Nakatani M, Kobayash Y, Sato S. (Crack-healing + proof test): A new methodology to guarantee the structural integrity of a ceramics component. Journal of the European Ceramic Society. 2002;**22**(1):121-128. DOI: 10.1016/S0955-2219(01)00236-9

[90] Ando K, Houjyou K, Chu MC, Takeshita ST, Takahashi K, Sakammoto S, et al. Crack-healing behavior of Si_3N_4/SiC ceramics under stress and fatigue strength at the temperature of healing (1000°C). Journal of the European Ceramic Society. 2002;**22**(8):1339-1346

[91] Van Tittelboom K, de Belie N, van Loo D, Jacobs P. Self-healing efficiency of cementitious materials containing tubular capsules filled with healing agent. Cement and Concrete Composites. 2011;**33**(4):497-505. DOI: 10.1016/j.cemconcomp.2011.01.004

[92] Jefferson A, Joseph C, Lark R, Isaacs B, Dunn S, Weager B. A new system for crack closure of cementitious materials using shrinkable polymers. Cement and Concrete Research. 2010;**40**(5):795-801. DOI: 10.1016/j.cemconres.2010.01.004

[93] Qian SZ, Zhou J, Schlangen E. Influence of curing condition and precracking time on the self-healing behavior of engineered cementitious composites. Cement and Concrete Composites. 2010;**32**(9):686-693. DOI: 10.1016/j.cemconcomp.2010.07.015

[94] Sahmaran M, Yildirim G, Erdem TK. Self-healing capability of cementitious composites incorporating different supplementary cementitious materials. Cement and Concrete Composites. 2013;**35**(1):89-101. DOI: 10.1016/j.cemconcomp.2012.08.013

[95] Sisomphon K, Copuroglu O, Koenders EAB. Effect of exposure conditions on self healing behavior of strain hardening cementitious composites incorporating various cementitious materials. Construction and Building Materials. 2013;**42**:217-224. DOI: 10.1016/j.conbuildmat.2013.01.012

[96] Li W, Jiang Z, Yang Z, Zhao N, Yuan W. Self-healing efficiency of cementitious materials containing microcapsules filled with healing adhesive: Mechanical restoration and healing process monitored by water absorption. PLoS One. 2013;**8**(11):e81616. DOI: 10.1371/journal.pone.0081616

[97] Ariffin NF, Hussin MW, Sam MAR, Lee HS, Khalid NHA, Lim NHAS, et al. Mechanical properties and self-healing mechanism of epoxy mortar. Jurnal Teknologi. 2015;**12**:37-44

[98] Luhar S, Gourav S. A review paper on self healing concrete. Journal of Civil Engineering Research and Practice. 2015;**5**(3):53-58. DOI: 10.5923/j.jce.20150503.01

[99] Cao QY, Hao TY, Su B. Crack self-healing properties of concrete with adhesive. Advances in Materials Research. 1880-1884;**2014**:919-921. DOI: 10.4028/www.scientific.net/AMR.919-921.1880

[100] Granger S, Pijaudier-Cabot G, Loukili A. Mechanical behavior of self-healed ultra high performance concrete: From experimental evidence to modeling. In: Proceedings of 3rd International Conference on Construction Materials: Performance, Innovations and Structural Implications (ConMat'05), 22-24th August 2005. Canada: Vancouver; 2005

[101] Van TK, Tsangouri E, Van HD, Belie ND. The efficiency of self-healing concrete using alternative manufacturing procedures and more realistic crack patterns. Cement and Concrete Composites. 2015;**57**:142-152. DOI: 10.1016/j.cemconcomp.2014.12.002

[102] Van TK, Gruyaert E, Rahier H, Belie ND. Influence of mix composition on the extent of autogenous crack healing by continued hydration or calcium carbonate formation. Construction and Building Materials. 2012;**37**:349-359. DOI: 10.1016/j.conbuildmat.2012.07.026

[103] Elmoaty A. Self-healing of polymer modified concrete. Alexandria Engineering Journal. 2011;**50**(2):171-178

[104] Zhong W, Yao W. Influence of damage degree on self-healing of concrete. Construction and Building Materials. 2008;**22**(6):1137-1142. DOI: 10.1016/j.conbuildmat.2007.02.006

[105] Yang Z, Hollar J, He X, Shi X. A self-healing cementitious composite using oil core/silica gel shell microcapsules. Cement and Concrete Composites. 2011b;**33**(4):506-512. DOI: 10.1016/j.cemconcomp.2011.01.010

[106] Huang H, Ye G. Self-healing of cracks in cement paste affected by additional Ca^{2+} ions in the healing agent. Journal of Intelligent Material Systems and Structures. 2014;**26**(3):309. DOI: 10.1177/1045389X14525490

[107] Xu J, Yao W. Multiscale mechanical quantification of self-healing concrete incorporating non-ureolytic bacteria-based healing agent. Cement and Concrete Research. 2014;**64**:1-10. DOI: 10.1016/j.cemconres.2014.06.003

[108] Sauvant-Moynot IV, Gonzalez S, Kittel J. Self-healing coatings: An alternative route for anticoorosion protection. Progress in Organic Coatings. 2008;**63**(3):307-315. DOI: 10.1016/j.porgcoat.2008.03.004

[109] Gonzalez-Garcia Y, Garcia SJ, Mol JMC. Electrochemical techniques for the study of self healing coatings. In: Hughes AE, Mol JMC, Zheludkevich ML, Buchheit RG, editors. Active Protective Coatings: New-Generation Coating for Metals. Vol. 233. Springer Series in Materials Science; 2016. pp. 203-239. DOI: 10.1007/978-94-017-7540-3

[110] Aparicio M, Mosa J. Electrochemical characterization of sol–gel coatings for corrosion protection of metal substrates. Journal of Sol-Gel Science and Technology. 2018;**88**:77-89. DOI: 10.1007/s10971-018-4785-9

[111] Aramaki K. An attempt to prepare nonchromate, self-healing protective films containing molybdate on iron. Corrosion. 1999;**55**(11):1020-1030. DOI: 10.5006/1.3283939

[112] Hughes AE, Yang S, Oezkaya B, Ozcan O, Grundmeier G. Physico-chemical characterization of protective coatings and self healing processes. In: Hughes AE, Mol JMC, Zheludkevich ML, Buchheit RG, editors. Active Protective Coatings: New-Generation Coating for Metals. Vol. 233. Springer Series in Materials Science; 2016. pp. 203-239. DOI: 10.1007/978-94-017-7540-3

[113] Lucca D, Hermann K, Klopfstein M. Nanoindentation: Measuring methods and applications. CIRP Annals - Manufacturing Technology. 2010;**59**(2):803-819. DOI: 10.1016/j.cirp.2010.05.009