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Study of quantification methods in self-healing ceramics, polymers and concrete – a route towards standardisation

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Abstract

During the past decades, research in self-healing materials has focused on the improvement in mechanical properties, making stronger materials, able to bear increasing solicitations. This strategy proved to be costly and in some cases inefficient, since materials continue to fail, and maintenance costs remained high. Instead of preparing stronger materials, it is more efficient to prepare them to heal themselves, reducing repairing costs and prolonging their lifetime. Several different self-healing strategies, applied to different material classes, have been comprehensively studied. When new materials are subject of research, the attention is directed into the formulations, product processing and scale-up possibilities. Efforts to measure self-healing properties have been conducted considering the specific characteristics of each material class. The development of comprehensive service conditions allowing an unified discussion across different materials classes and the standardization of the underlying quantification methods has not been a priority so far. Until recently, the quantification of self-healing ability or efficiency was focused mostly on the macroscale evaluation, while micro and nanoscale events, responsible for the first stage in material failure, received minor attention. This work reviews the main evaluation methods developed to assess self-healing and intends to establish a route for fundamental understanding of the healing phenomena.

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1. Introduction

Throughout the years, a major goal of the materials sciences is in the optimization of the material's reliability and resilience, and to ensure minimal risk of failure during service life. This is particularly important for applications with demanding service conditions, where maintenance operations and material substitution can be difficult, costly and time consuming. For instance, some coating materials are so susceptible to damage that they require frequent repairing and replacement. This not only affects the reliability and durability of materials, it also has a strong environmental impact. Recently, the strategy to prevent damage and prolong lifetime resulted in a new approach - the development of self-healing properties in materials (Zhang et al., 2013: 5).

Self-healing materials have been intensively investigated in the past ten years, as shown by the increasing number of patents issued and publications in the field. Since 2005, were published more than 16000 papers (Figure 1) and about 500 patents (Figure 2) related to self-healing materials, more than 2/3 of which within the past five years. The field of self-healing can be divided in several sub-domains depending on the material, mechanism and repairing strategy. Polymers (bulk and coatings) are by far the most studied and most of the commercially available materials belong to this material class (AkzoNobel, 2013; HIT, 2013; Intergard, 2013; Autonomic and Materials, 2013) . Considering the still limited number of commercial products available on today's market, it is obvious that further fundamental research is necessary to further promote an effective knowledge transfer from the scientific community to industry.

One important step in the evolution of a broader picture of the wide opportunities in improving the self-healing and resilience of materials, is the development of a common set of definitions valid across the material's classes (Awaja et al., 2009; Bergman and Wudl, 2007; Fischer, 2010; Hearn, 1998). The establishment of a suitable definition for the quantities and mechanisms in the context of self-healing is an important prerequisite to allow an interdisciplinary discussion and will advance the commercial breakthrough of more products based on self-healing materials.

Damage during life service should be considered as an accumulation of microdamages that ultimately lead to catastrophic failure. When a material is damaged, one or more cracks start to develop at the microscopic level (Huang et al., 2013; Kawaguchi and Pearson, 2004; Darabi et al., 2012). These cracks tend to propagate via a coalescence effect and can cause the material rupture. Based on this common starting point, the path is open to accept the idea of partial recovery or regeneration (Stuart et al., 2010). In an ideal self-healing material, the damage itself or the originating stress serves as the trigger for the recovery mechanism (Elmoaty, 2011; Hamilton et al., 2012a; Yabuki, 2011). In other cases, the healing process is activated by an external trigger (temperature, electrical stimulus, light, or other). This activation process is influenced by the location, where the damage occurs and healing time, which depends on the damage extension (Burattini et al., 2010). It can involve molecular activation, transport processes, and/or chemical reactions, which ultimately results in the restauration of the original properties at the damaged site (Wiggins et al., 2013).

Different classification methods have been developed, depending on the material class and application (Hager et al., 2010). Healing strategies can be classified in two separate categories: non-autonomic and autonomic. In the first, the damage regeneration depends on an external stimulus, such as light, heat or electric current (Wojtecki et al., 2011). The external energy source can either be manually applied, or is already present as a consequence of the service conditions (materials used in high temperature environments or exposed to solar light) (Billiet et al., 2013). On the other hand, autonomic healing occurs without external triggering – a form of energy dissipation caused by the damage or its origin is already enough to enable the healing process (White et al., 2001). Further, the self-healing effects can be divided in intrinsic or extrinsic mechanisms, depending on how the regeneration process is developed, the material recovers from damage as consequence of chemical or physical interactions between the crack surfaces (intrinsic) (Hart et al., 2013), or the repair is achieved by the activation of a healing agent (in the form of microcapsules, hollow fibres or vascular network) (Mauldin and Kessler, 2010).

Considerable advancement was achieved in the understanding and optimization of the self-healing behaviour of ceramics, polymers, fibre reinforced polymer (FRPs) and concrete during the last decades (Zwaag et al., 2007), and novel strategies have been developed and will be briefly discussed in the following sections of this work. In parallel, numerous methodologies for the assessment of self-healing capabilities have been developed for each material class (Table 1). A main objective of this work is to give a comprehensive overview on the different healing and quantification methods currently employed for the different material classes, addressing as well macroscopic as well as microscale assessment of self-healing.

A number of fundamental parameters must be considered: (i) the stimulus (if any) and time required to heal the material, (ii) the number of breaking and healing cycles which the material can sustain without loss of properties, and (iii) the extent to which the material may be re-healed – taking account relevant mechanical properties such as tensile modulus, elongation at break, fatigue-resistance and physical parameters like colour or transparency. In addition there is the practical requirement that, ultimately, the material system should be inexpensive and readily processable to enable it to move from being a purely research material to one with a significant impact on everyday life. With such a diverse range of parameters to be optimised it is clear that many formidable challenges remain, but that, as a consequence, tremendous potential exists for breakthroughs in the design and development of healable materials over the coming years.

Hence, when self-healing is appraised, a range of different parameters needs to be considered: type of stimulus, healing time, maximum amount of healing cycles the material can tolerate and degree of re-healing, considering the material ideal properties (Zhu et al., 2014; Pacheco et al., 2014; Chen and Guan, 2014). Additionally, other aspects beyond physical parameters have to be judged, like production cost and easy processing.

2. Self-healing in polymers and fibre reinforced polymer (FRPs)

Polymers and FRPCs are by far the most studied material classes with self-healing properties. Because polymeric systems can be easily modified or blended, and the temperatures required to induce mobility are relatively low, its functionalization can be achieved with a high degree of success (Hart et al., 2013; Mauldin and Kessler, 2010; Barner-Kowollik et al., 2012).

Healing can be assessed by evaluating restoration of one or more properties. Although the goal is to achieve full recovery, self-healing materials can be considered successful if they exhibit 80% or more for healing efficiency (Brown et al., 2005). When healing is estimated through crack closure, efficiency is determined by how successfully the crack has been repaired (Brown et al., 2006).

2.1. Crack filling by polymerization reaction

A frequent strategy to achieve self-healing in polymeric systems involves the incorporation of single or binary compounds, formed by an agent and a catalyst, that react immediately after the damage leading to crack filling (Blaiszik et al., 2010; Jin et al., 2012). As exemplified in

Figure 3 (Samadzadeh et al., 2010), the additives remain inactive and stored inside containers (e.g. capsules, hollow fibres), and as soon as these containers rupture around the damaged site, the two components react, leading to a solidification and thus repair of the damage. Capillary forces drive the healing agents to the area of interest (Mangun et al., 2010). Drawbacks include a possible loss of mechanical performance caused by the incorporation of the capsules, and the restriction to one healing per damaged site, because each location can only be healed one time. When damage occurs in the exact same spot again, there will be no capsules to re-heal the site. (Pacheco et al., 2014; Wu et al., 2008).

Fibre reinforced polymer composites (FRPC) with self-healing properties are obtained by using healing agent incorporated into hollow fibres inside the polymeric matrix (Kousourakis and Mouritz, 2010; Zwaag et al., 2014). This way, a higher amount of agent, a prolonged healing ability and a simultaneous reinforcement of the material structure can be achieved. Wu et al developed a new type of reinforcement using hollow nano-fibres with increased performance, particularly at interfacial damage level (Wu and Yarin, 2013). To overcome the limited number of healing cycles, microvascular networks have been proposed, that similar to blood vessels, enable an external refill (Chen et al., 2013; Olugebefola et al., 2010; Phillips et al., 2011). These networks are complex in their production, raising the interest to develop cost effective alternative techniques (Hamilton et al., 2012b).

2.2. Chemical/physical healing by reversible bonds

Chemical and physical interaction methods differ from the above (crack filling effect) as they are not relying on encapsulation and on the transport of species through the material to the damaged site. In contrast, healing is achieved by self-assembling mechanisms based on specific chemical and/or physical interactions that lead to crack closure (Wu et al., 2008).

2.2.1. Ionomers

Self-healing Ionomers take advantage on the phase separation of ionic groups within non-polar polymeric matrices, playing an important role in controlling their structural properties (Hohlbein et al., 2013). The principle is mainly investigated for semi-crystalline or elastomeric polymers, and is promoted in the occurrence of local heat. Main chain flexibility accelerates the process by chain interdiffusion. In the case of ballistic damage, it was found that a high ionic content does not necessarily result in higher self-healing efficiency (Nellesen et al., 2010; Kalista et al., 2007).

2.2.2. Covalent bonds

Theoretically, it is similarly possible to produce repeated self-healing processes in polymers by the employment of reversible covalent bonds. The concept is based on the assumption that failure within polymer materials happens along the weakest covalent bonds, and can in general involve main chain links or the crosslinks. For polymers that repair via bond reconstruction, the healing process relies mostly in the ability to place sacrificial, relatively weak bonds, prepared to recombine and reconstruct the structure of the virgin polymer, after the damage.

The reverse reaction can be triggered by external stimulus (temperature, stress, electrical current) (Kloxin et al., 2010). Among these, temperature is a common external trigger for polymers with reversible covalent bonds, in particular in systems based on the Diels–Alder/retro Diels–Alder reaction (Scheltjens et al., 2013; Yoshie et al., 2011). Up to date, a transfer to market is hindered by the high scale-up costs of the monomer synthesis (Bai et al., 2013).

2.2.3. Supramolecular forces

Mendable polymers (“mendomers”) are engineered to integrate low strength bonds that break when subject to stress. After macroscopic damage, an external trigger is applied to promote the polymerization process (Herbst et al., 2013). The most common approach is to provide heat as an external trigger however exposure to light can also be used in low molecular mass polymers (Burnworth et al., 2011). Meure et al. established that the healing mechanism is thermally activated and the release of the agent is achieved by a pressure deliver system (Meure et al., 2012). The healing efficiency in these materials is usually interdependent on the base of the number and length of the available chains.

Polymers prepared via supramolecular assembly have proven to show complete repair of the damaged areas, based in the recombination of non-covalent interactions, like hydrogen bonding or π-π stacking (Xu et al., 2012; Fox et al., 2012), or metal-ligand bonds (Varley et al., 2010). However, material properties such as polymer strength are compromised by the presence of weak dynamic bonds (Cordier et al., 2008; Capelot et al., 2012b; Garcia, 2014; Wool, 2008).

2.3. Mechanochemical activation

Mechanochemically active units start a local polymerization or crosslinking process as soon as the material is subject to stress or damage. This is an emergent topic in self-healing polymers and very few results were published so far. The active unit, designated as mechanophore, e. g. is able to form radicals that initiate fast cross-linking processes before the material displays complete failure (Hong et al., 2013; Lee et al., 2010). The polymer is shown to display a positive response to stress induced by ultrasound activation however, the microscopic response to mechanical load remains unknown, and its translation to the bulk material remains unsolved (Davis et al., 2009).

3. Self-healing in concrete

Voids and damage in concrete, caused by the preparation process and service solicitations (forces), can cause cracks that tend to propagate with time. These cracks can be a potential risk of failure for the concrete structures. Water ingress, causes rebar exposure via capillary pores or cracks, reducing considerably the concrete life span (Pacheco et al., 2014). Cement materials can exhibit, up to a certain extent, a natural ability to self-repair due to long-term hydration process. The hydration process can continue for an extended interval of time after the cure, and thus some initial cracks can be naturally closed, especially in humid environments. This natural ability to self-heal can be boosted by encapsulated bacteria or specific additives in engineered self-healing of concrete (Tittelboom and Belie, 2013).

3.1. Microcapsule and fibre encapsulation of the healing agent

Similar to polymer and composite matrices (see section 2.1), the development of capsular or microvascular systems carrying suitable self-healing agents can be applied to concrete; e. g., hollow fibres filled with liquid healing agents like methyl methacrylate are introduced. The damage and the originated crack force the fibre to break and release the agent (Figure 4) (Tittelboom and Belie, 2013). When the healing agent is released, the space created by the crack is filled with polymerization products and the concrete is repaired (Lark et al., 2011). The healing efficiency obtained with these systems is relatively low since the amount of healing agent released might be insufficient to fill the damaged area, with cracks that can be up to 200 μm. When the healing agent is externally loaded by refill, a possible depletion can be effectively avoided, however the system gets more complex by the requirement of manual intervention (Sangadji and Schlangen, 2013; Escobar et al., 2013).

3.2. Bacteria

One prominent approach in the self-healing of concrete is the introduction of encapsulated bacteria that are able to initiate calcium carbonate precipitation (Figure 5) (Wu et al., 2012), and thus to fill the gap caused by the damage (Jonkers et al., 2010; Muynck et al., 2008). To initiate the healing only after damage, the bacteria are immobilized in capsules or fibres (Wang et al., 2012; Wiktor and Jonkers, 2011). Another problem is the distribution of the containers inside the matrix, in view of concrete being a non-homogeneous material with an extended range of particle sizes and pore sizes (Wu et al., 2012).

3.3. Shape memory materials (SMM)

Shape memory materials are able to recover the original shape after damage or deformation upon application of an e. g. electrical stimulus, temperature or humidity increase (Leng et al., 2011). When shape memory polymers are introduced into a concrete matrix, they can be employed to close cracks by expansion (Jefferson et al., 2010; Zwaag et al., 2009). The use of SMM is based on the assumption that early stage cracks in concrete are caused by shrinkage and thermal effects already during the cure period. Since the proposed SMM is temperature-triggered, its expansion leads to closure of the cracks. The applicability of this approach is limited to macro-sized cracks, and depends on the exposure of the concrete to heat.

3.4. Super-absorbent polymers (SAP)

Hydrogels constituted from hydrophilic cross-linked polymers carrying ionic groups, are able to absorb a high amount of liquid under intensive swelling producing an insoluble gel. The SAP is introduced into the concrete matrix, and if after crack formation humidity enters the structure, the gel swells and closes the void (Snoeck et al., 2012).

3.5. Additives promoting concrete hydration

Certain cement admixtures can endure further hydration after the initial curing period, a behaviour that allows for an intrinsic self-healing (Huang and Ye, 2015). It is found that the application of fly ash, mixtures of SiO_2 and Al_2O_3, combinations of expansive agents, lime and some carbonates ($NaHCO_3$ or Na_2CO_3) in cement admixtures can promote the long-term hydration phenomena granting the concrete with self-healing capabilities (Ahn and Kishi, 2010; Termkhajornkit et al., 2009). All these additives proved effective for promoting the recrystallization of concrete, accompanied by crack filling, and assure an effective self-healing in a short period.

A different self-healing strategy was studied by Qian et al. using fibres in a cementitious composite with blast furnace and lime powder. Uniaxial tensile loading was applied to the samples and healing was achieved through further hydration by water curing (Huang et al., 2013; Qian et al., 2009).

4. Self-healing in ceramics

When the first cracks are formed inside a ceramic matrix, it quickly suffers catastrophic failure even when subjected to subcritical loading, due to its brittle nature (Suresh et al., 1990; Ayatollahi and Aliha, 2011). In addition, the presence of inner porosity is often another cause of reduced strength in ceramics. Therefore, the development of self-healing properties in ceramics focused in repairing structural defects to increase durability (Houjou et al., 2010). Potential application for self-healing ceramic oxides as protective coatings for metals has been investigated (Wang et al., 2013b). The relevant interactions in ceramics are ionic and covalent in nature, and thus, contrary to polymers, their remending accompanied by solid-state diffusion requires high activation energy. In consequence, it is difficult to achieve self-healing in ceramics below 1000 °C. Accordingly, current research in ceramic materials is based always in high temperature healing mechanisms. An optimization of the self-healing ability in ceramics is thus relying on structural modifications at the microscopic level and the understanding of the underlying mechanisms (Harrer et al., 2012).

The healing process is guided by four main routes (Greil, 2012):

- crack closure caused by controlled sintering at elevated temperatures leading to solid state diffusion,
- crack filling promoted by viscous flow of a glass phase,
- filling the damage with products from an oxidation reaction (Figure 6) (Greil, 2012),
- eutectic melt or phase transition that can lead to particle rearrangement in multiphase materials.

4.1. Healing through oxidation products

Silicon carbides are used for specific engineering applications, like engines and low friction tools, due to their excellent mechanical properties but they are susceptible to cracks that can compromise their application. Silicon carbide composites can exhibit good healing capabilities and several compositions have been developed with success in the last decades. After damage, heat treatment leads to the formation of oxidation products that fill the crack by volume increase, thereby ideally restoring the original material properties. SiC combined with Y_2O_3 stabilized zirconia, Si_3N_4, or mullite ($Al_2Al_{2+2x}Si_{2-2x}O_{10-x}$), proved to be efficient compositions for self-healing ceramics (Nam and Hwang, 2012; Magnani et al., 2010; Jung et al., 2009; Takahashi et al., 2010).

4.2. Oxidation of A elements in MAX phase systems

MAX phase ceramics constitute a special group of ceramics with very specific characteristics. They exhibit good electrical and thermal conductivity, low hardness and high tolerance to damage – comparable to metals. At the same time, they present oxidation and corrosion resistance, high elastic modulus and good thermal shock behaviour, characteristic of ceramic materials (Eklund et al., 2010). The MAX designation is directly related to its molecular composition and stands for an abbreviation of the general formula $M_{n+1}AX_n$. They are constituted by an early transition metal M (Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta), an element from the A group (Al, Si, P, S, Ga, Ge, As, In, Sn, Tl, Pb) and the X element C and/or N. Possible phases are M_2AX (211), M_3AX_2 (312) or M_4AX_3 (413) (Sun, 2011).

The initial process to obtain these materials involved cost-intensive reactive sintering processes, and was not attractive to be scaled up (Wang et al., 2013a). Recently, a novel preparation technique by cold pressing followed by pressure-less sintering was developed, that may find application in industry (Yang et al., 2013a). In addition, MAX phase thin films can be prepared by chemical vapour deposition (CVD).

The healing process in MAX phase ceramics is based on the oxidation of the A elements with environmental oxygen at elevated temperatures. The oxidization process is accompanied by volume increase, leading to filling of the crack space. Since there is a limited supply of the A element inside the matrix, the healing efficiency tends to decrease with time. Attempts have been made to prolong the healing life span using for example nano-sized powders that increase the surface energy(Wang et al., 2013a). Yang et al. investigated the effect of oxide scale growth in the healing efficiency of Cr_2AlC ceramic (Yang et al., 2013a). They demonstrated that healing results from new oxide growth in the grain boundaries.

5. Healing quantification

The ability for self-healing of a given material is often referred as the ability to recover a specific property relative to the virgin or undamaged material, designated as healing efficiency η (Mauldin and Kessler, 2010). In order to result in useful interpretation, a number of factors need to be considered. In particular, the addition of a healing agent to a material formulation can be of impact on its mechanical properties in relation to the virgin material (without healing agent) (Murphy and Wudl, 2010). Under these circumstances, the efficiency assessment needs to take into account the effect caused by the presence of the additive (Billiet et al., 2013; Xu et al., 2012).

Self-healing efficiency can be determined by comparing the value obtained for the undamaged sample (f_{virgin}) with the healed sample (f_{healed}) (eq. 1) (Mauldin and Kessler, 2010).

$$\eta = \frac{f_{healed}}{f_{virgin}} \times 100 \qquad (1)$$

Due to the healing agent impact, however, this evaluation can retrieve results higher than 100%, which can be misrepresentative (Hatami Boura et al., 2012; Plaisted and Nemat-Nasser, 2007). In a variation of this simple definition, the healing efficiency takes into consideration the original properties of the virgin material and the modifications caused by introducing the healing agent, leading to the comparison of the healed sample property to that of a non-healed and undamaged probe (equation 2) (Mauldin and Kessler, 2010).

$$\eta = \frac{f_{healed}}{f_{virgin}} \times 100 \qquad (2)$$

The spectrum of materials properties that can be either fully or partially restored in a self-healing process is manifold, ranging from mechanical over optical, haptic or barrier properties. Thus, to select the appropriate assessment method for the quantification of the self-healing properties, the nature and the extension of the damage need to be taken into consideration in the first place (Huang et al., 2013). In the present research, a major focus is found in the mechanical restauration of materials by self-healing properties, pointing also to the importance of the length scales of the involved processes. The applied damage can be just enough to create microcracks with a measurable size before efficient healing, or it can be fast and extensive, requiring quick action to prevent the catastrophic failure of the sample (Fox et al., 2012). It is therefore necessary to develop effective and reliable methods on different length scales to quantify the healing properties and to understand the underlying mechanisms

(Yoshioka and Nakao, 2015). It is understood that for the ideal self-healing material, property recovery should occur on an early point of time after damage occurrence. Micromechanical tests can provide relevant information about the effectiveness of early stages damage repair (Ahangari and Fereidoon, 2015),macroscopic quantification methods still hold the advantage of easier standardization compared with microscale methods however, they are less efficient to assess nano and micro-crack healing (Zhu et al., 2015).

5.1. Bulk polymers and composites

Recovery from fracture is one important aspect for the evaluation of healing efficiency in polymers and composites. The tests conducted to evaluate recovery from damage (impact, fatigue, quasi-static fracture, among others) can be classified as Mode I (opening) or Mode III (tearing) fracture evaluation (see Figure 7) (Jin et al., 2013; Majchrzak et al., 2012; Lawn, 1975).

In a Mode I fracture process, the simulated macroscopic fracture is performed similar to the crack development as naturally occurring at the microscale under repeated stress and/or fatigue. Tests performed under these conditions are useful to understand the material failure under real conditions. The sample geometry is of particular importance when evaluating the mechanical healing efficiency and its choice should take into account which type of cracks the material develops under stress. Among the proposed geometry, the tapered double-cantilever beam (TDCB) geometry (Figure 8) has been proposed and successfully been employed in bulk polymers with non-linear fracture characteristics, as it does not display a critical crack length (Jones and Dutta, 2010). In this specific configuration, fracture toughness is independent of crack length. The fracture load is measured before and after healing, and the load-based healing efficiency is determined according to equation 1 or 2 (Mangun et al., 2010; Kirkby et al., 2009). With this geometry, the crack development can be readily controlled, giving access to an additional optical examination of the crack area after applying damage, and after healing (Hatami Boura et al., 2012; Yuan et al., 2009; Rule et al., 2007).

For the assessment of the self-healing characteristics of thermosetting resins and composites (Hayes et al., 2007), compact tension (CT) test specimens (Figure 9) have been proven convenient, as demonstrated on i.e. epoxy resins containing microencapsulated self-healing agent (Murphy and Wudl, 2010). The shape is wide enough to enable crack development without complete separation. An additional hole, drilled in the center of the sample, stops the crack growth and thus ensures a controlled and reproducible damaging and healing process (Chen et al., 2003; Peterson et al., 2012). The samples are tested until crack initiation, unloaded, healed and finally tested after repairing.

For epoxy matrices, fracture toughness is commonly determined using the width-tapered double cantilever beam (WTDCB) geometry (Figure 10) (Hatami Boura et al., 2012). This shape can provide measurements that are independent from crack length (Jin et al., 2011). Another geometry employed for the fracture toughness of mendable epoxy resins is the single edge notched beam (SENB) setup (Meure et al., 2012; Meure et al., 2009). On the other hand, the crack propagation under fatigue loading can be addressed by double cleavage drilled compression (DCDC) experiments (Hamilton et al., 2012a). Thereby, the crack size can be readily controlled with an accurate regulation of loading vs. displacement, and the surfaces are easily aligned before the healing process (Plaisted et al., 2006).

The occurrence of delamination cracks between fibre and matrix constitutes one of the major problems in fibre reinforced polymer composites. This problem that can only be addressed to a limited extend by surface compatibility, can be reduced using self-healing agents, and healing efficiency is evaluated by Mode I interlaminar fracture tests (Pingkarawat et al., 2013). The extension and efficiency of the delamination toughening can be determined by fracture testing with a double cantilever beam (DCB) (Norris et al., 2011; Yang et al., 2012). Hereby, a delamination crack created inside the material is healed under controlled temperature, and the fracture toughness *(G)* is usually the base for healing efficiency evaluation (Eq. 3) (Pingkarawat et al., 2013).

$$\eta = \frac{G_{healed}}{G_{virgin}} \times 100 \qquad (3)$$

Some fibre-reinforced and sandwich composites, due to their specific applications (aircraft, spacecraft, etc.), are especially vulnerable to damage impact. To determine the efficiency of self-healing systems, these materials are investigated in terms of compression strength after impact (Williams et al., 2009). These types of tests can be considered effective to determine healing efficiency in large-scale damages that can reoccur frequently during life service (Chen et al., 2013). To assess the superficial damage in such composites, mixed-mode indentation tests were used to determine the sealing efficiency (Moll et al., 2010). Hereby, the focus was set to the superficial sealing capabilities instead on the recovery of the mechanical properties.

Fibre-reinforced polymer composites are further studied by Mode II interlaminar fracture testing. This evaluation can be conducted with different types of tests with distinctive types of sample configurations: end notched flexure (ENF), end loaded split (ELS), four-point bend end notched flexure (4PBENF), and over-notched flexure (ONF) (Wang et al., 2009). The effect of friction with this type of tests poses a major problem to determine fracture toughness. This can constitute an obstacle for the evaluation of self-healing properties. Norris et al. compared both Mode I and Mode II methods, and concluded that mode II crack propagation was less stable. They found that crack can be redirected under Mode II when vascules are orientated transverse to the crack propagation path(Norris et al., 2011). A close analogy to the actual application was also searched by Kousourakis et al. studying a mixed mode fracture test specifically designed to evaluate T-joint tensile strength in composites (Kousourakis and Mouritz, 2010). The specimens were subjected to stress prior and after healing.

Mode III fracture tests performed by tear and/or shear tests displayed difficulties concerning the inconsistency of the crack path (Keller et al., 2007), leading to limited reproducibility of the tests and the quantification of healing (Capelot et al., 2012a). Another phenomenon that has to be dealt with in shear tests is self-adhesion that cannot be separated from the healing effect and thus may cause misleading results (Awaja et al., 2009; Maes et al., 2012).

When fracture toughness is being evaluated, Mode I fracture is of high importance for materials with elastic-plastic behaviour or an extensive plastic area in front of the crack tip since it is highly sensitive to crack instability. Mode II is used to determine the critical energy release however unstable crack growth when the sample is in loading can be a disadvantage. ASTM already created standards for Mode I loading with cantilever beam (DCB) (ASTM, 2001), for pure Mode II with end notch flexure (ENF) (ASTM, 2014) and a standard that measures fracture toughness for different combinations of Mode I and II loading (ASTM, 2006). Though several authors are already using them, further studies on the applicability of these standards with self-healing materials are required (Everitt et al., 2015).

Several authors chose macroscopic cutting as a technique to evaluate self-healing (Figure 11). The sample is completely separated with a razor blade or scalpel, and both surfaces are attached again by applying manual or controlled pressure (Patrickios et al., 2010). Although widely applied, this evaluation technique can be considered among the most unreliable ones. There are major concerns with respect to the reproducibility of the cut, and in many cases the pressure applied for the self-healing process is insufficiently quantified and controlled. In addition, the state of complete separation fails to simulate the real service conditions, where complete material rupture cannot be tolerated. In addition, it is questionable how far the findings can readily be translated to the healing of microscale cracks, as the self-healing process in polymers is generally strongly influenced by the respective surface energy (being a function of surface history – thus its evolution), and the number of broken chains available in both surfaces. What is more, the size of the cracks determines the evolving surface morphology. These considerations already demonstrate that microcracks formed during service are only of very limited comparability to a single cut performed by a razor blade (Cordier et al., 2008; Yamaguchi et al., 2007).

A modified compression test has been developed as an attempt to evolve from the blade cutting method to a more accurate technique, and was applied to supramolecular rubbers. Although the method principally holds potential for useful quantification, there are some issues related to the testing conditions of the low T_g rubbers that need to be addressed before considering the method suitable for healing quantification (Wang et al., 2009).

In another approach, specimens are crushed by compression, and are healed and retested to determine healing efficiency on the base of the compression strength (Martín et al., 2012). Similar to the discussion above, the tests comprise a complete specimen destruction, and thus do not deliver useful information concerning its performance during service conditions.

5.2. Polymeric coatings

While in bulk materials the emphasis is given to function and performance under stress, in coatings other damages like erosion (mechanical damage) and corrosion (chemical degradation) play a more important role. Typically, corrosion and erosion occur simultaneously, thereby increasing the coating degradation rate significantly. It is not surprising that the methods to evaluate polymeric coatings are distinctive from the ones employed for bulk systems.

In order to simulate the service performance and to get a quantitative or qualitative information on the effective lifetime of a coating, accelerated impact erosion tests are performed This simulation, however, displays several limitations in the comparability to the service conditions. As an example, the impact angle determines the extent of the damage and cannot be controlled in real conditions. In addition, the accelerated erosion test fails to simulate the corrosion effect due to the different time scale (Yabuki, 2011).

The degradation process in coatings begins at a molecular level, when molecules dissociate and bonds break. In a second level, networks are affected and the first microcracks start to appear opening the path for microscale corrosion. Only after a long period of microscale damage is possible to observe delamination, scratches, and surface rupture. Many of the methods employed today to evaluate self-healing in coatings only address the later stage, when the important events occur during the first and second one.

To determine healing efficiency in coatings, a simple and broadly applied method involves cutting the sample with a razor blade (Figure 12) (Yoon et al., 2012), followed by ESEM (environmental scanning electron microscope) or optical observation, before and after healing (Zhao et al., 2012). The cutting technique is often used in corrosion tests. After the cut non-healed and healed samples are immersed in a saline solution to accelerate a possible corrosion (Hatami Boura et al., 2012; Nesterova et al., 2012; Samadzadeh et al., 2011). Alternatively, the oxidation resistance of the coated surface can be evaluated by impedance spectroscopy. However, it needs to be pointed out that the damage provided by a razor blade causes a high degree of uncertainty in the quantification due to irreproducibility of the cuts, and furthermore does not accurately simulate the combined microdamage/corrosion process that typically occurs during service life.

As the macroscopic level of damage is strongly dependent of the events occurred during the molecular and microscopic stage, only the application of a reproducible microscale damaging method for quantification in the laboratory will make it possible to assess the healing process in coatings (Sauvant-Moynot et al., 2008). As an alternative, a modified 3-point bending method to induce superficial microcracks has been developed (Zhang et al., 2012). After healing, the microcracks were examined with an optical microscope and the samples were subjected to electrochemical corrosion. This method can provide a qualitative evaluation of micro damaging in coatings. Further, microscratching with a nanoindenter can provide qualitative data regarding healing efficiency. However, in both cases, a quantification of the healing efficiency cannot be achieved (Bertrand-Lambotte et al., 2001). In this situation, the healing is merely assessed by visual inspection, or by indirect measurements of properties (water vapour transmission and permeability). Since these properties are affected by other characteristics of the coatings (adhesion to substrate, porosity and microstructural defects) and not only by the healing, a qualitative evaluation cannot be attained in this manner (Liu et al., 2008).

Recently, a 4-point bending test coupled with an acoustic emission sensor was proposed to detect crack formation before healing, and to determine crack reopening after treatment (Toohey et al., 2009). As the mode I fracture toughness *K* is directly correlated to the energy released, the healing efficiency was determined according to equation 4.

$$\eta = \frac{K_{healed}}{K_{virgin}} \times 100 \qquad (4)$$

For a proper functioning of protective coatings, adhesion to the substrate is one important aspect. It is frequently observed, that by introduction of nano- or microcapsules into polymeric films, the adhesion strength is significantly reduced, and that this can compromise the durability of the self-healing coatings (Samadzadeh et al., 2011). Under this aspect is generally observed that the problem is attenuated with smaller particles (Hatami Boura et al., 2012). In this respect, also the sometimes increased thickness of self-healing coatings may cause drawbacks for the quantification of the adhesion strength, as adhesion tests performed according to the standard procedure are limited to coatings with a thickness below 250 µm (Hatami Boura et al., 2012; Sauvant-Moynot et al., 2008).

5.3. Cement and concrete

Cracks in concrete are the lead cause for mechanical failure as they reduce the mechanical strength of the cement matrix and expose the reinforcing components to corrosion. The mechanical strength and the permeability of the material are thus also the key parameters for durability. In order to address this with respect to self-healing effects, the standard compression and flexural tests are applied to the material in a controlled way in order to initiate cracks inside the matrix. After damaging, the samples are subjected to the healing process and then retested with the same procedure (Tittelboom et al., 2011).

To determine the stress of initial cracking, the bending deformation needs to be carefully controlled. Some authors apply a notch in the middle point that helps to control crack initiation (Jefferson et al., 2010). Although some authors choose the 3-point bending, 4-point bending protocol is known to be more effective to develop initiation cracks without causing failure (Qian et al., 2010; Sahmaran et al., 2013; Sisomphon et al., 2013). In these type of tests, crack development and the breakability of the capsules needs to be detected using complementary methods like acoustic emission analysis (Van Tittelboom et al., 2015). In another work Tittelboom et al. attached a linear variable differential transformer to the bottom of the sample (Figure 13) (Tittelboom et al., 2011), which improved the accuracy for crack detection (Tittelboom et al., 2012). Other researchers applied ultrasonic pulse velocity to determine the formation of cracks during bending, and to investigate the influence of damage degree in concrete healing (Elmoaty, 2011; Zhong and Yao, 2008).

Limited lifetime due to the corrosion of the steel reinforcement in concrete is known to be strongly related to internal cracking followed by exposure of the steel reinforcement to the external environment. A detailed permeability analysis is thus generally recommended in order to evaluate how effective self-healing concrete can protect steel reinforcement from corrosion (Sisomphon et al., 2012). Different environments can be using different permeation fluids (chlorine or water) and the temperature (freeze/thaw simulation) to approach more accurately the real service conditions (Sahmaran et al., 2013; Yang et al., 2011b). However, these laboratory tests still fail to simulate the combined corrosion and erosion effect present in some specific applications, for example in aggressive maritime environments.

5.4. Ceramics

Advanced ceramics are often susceptible to crack damage caused by mechanical and thermal stress during its lifetime, a main reason being their brittle nature. For the same reason, it is difficult to create controlled cracks within ceramic materials or coatings. Indentation is an efficient method to develop micro damaging without causing material failure, and in consequence, indentation is the most frequent quantification method found in literature (Le Bourhis, 2011). The test is conducted using either Vickers or Knoop indents, and samples are heat treated after damage. For quantification, the pre and post-healed indent is observed with optical and microscopic techniques (Nam and Hwang, 2012). The healing efficiency is measured in terms of crack closure, where the control samples are compared with the healed specimens. As an effort to improve healing assessment in ceramics, some authors complemented indentation with bending tests to determine the strength of crack closure (Nam and Hwang, 2012). The specimens, damaged by indentation, were compared and evaluated in terms of crack propagation (Li et al., 2012). Gao et al. studied the healing efficiency in a ceramic coating in terms of adhesion by performing tensile tests (Gao and Suo, 2011). The correlation between healing time and residual stress is an important parameter for coatings subjected to thermal shock (Gao and Suo, 2010).

The conventional methods to measure the bending strength consider mostly perpendicular forces in order to avoid the influence of defects caused by specimen preparation. During their service life, ceramics that are once exposed to thermal shock can develop cracks in any direction. Harrer et al. applied a modified method for testing ceramics; the biaxial ball-on-three balls (B3B) test (Harrer et al., 2012). A specimen with a disc shape is positioned on three balls and centrally loaded by a fourth ball to simulate real service stress distribution (Figure 14) (Börger et al., 2004). Since the tests are performed at room temperature, the real effect of the thermal stress is not exactly reproduced, nevertheless the test is of potential for a reliable quantification of self-healing processes in ceramics.

When ceramic oxides are considered for structural applications, controlled damage and healing cycles need to be performed under mechanical and thermal stress. It is thus required to develop a method that evaluates the healing capabilities at elevated temperatures to assure the structural integrity of the components in service conditions. Usually though, the tests are performed at room temperature, and only the healing process is performed in real service conditions in terms of temperature, oxidation, and pressure, when the material is not under stress. As the behaviour of a ceramic material in terms of mechanical performance and oxidation can differ dramatically between ambient temperatures and typical service conditions above 1000˚C, a convenient meaningful method for the quantification of self-healing efficiency in ceramics is highly searched. In particular, local melting and phase transformations can alter the internal structure influencing the mechanical performance of the ceramics (Yang et al., 2011a). Ando et al. developed a testing methodology to determine self-healing processes and structural integrity of ceramics at elevated temperatures (1300˚C), and compared the results with those obtained at ambient conditions, demonstrating the importance of this approach (Ando et al., 2002).

The study of damage and healing processes at elevated temperatures is of particular importance for MAX phase ceramic materials, since, for a considerable number of compositions, the phase diagrams are not yet established, and the potential application areas and thus service conditions are not even completely determined – there are no commercially available products yet (Eklund et al., 2010). Similar to other ceramics, the self-healing process in MAX phases is determined by (nano) indentation, the cracks are characterized by SEM, and the mechanical strength of original, damaged and healed specimens is compared by 3 or 4-point bending (Högberg et al., 2005). Although the healing procedure and its outcomes can be compared for different temperatures, times and atmospheres, the actual mechanical tests are in almost all cases conducted at ambient conditions (Li et al., 2013; Yang et al., 2013b).

6. Standard procedure and parameter set for healing quantification

The expected upcoming key step in the development of the various concepts for self-healing materials is their transfer from the laboratory to commercial applications. Currently, only few materials succeeded in this objective and were implemented as real-world product, among these one can find a battle jacket using self-healing technology and a car coating (HIT, 2013; AkzoNobel, 2013).

The careful review of the currently employed approaches to quantify the efficiency of a self-healing process illustrates that the methods mostly concentrate on the macroscopic level, at least as far as the mechanical restoration is involved.

Even if the ultimate goal behind the development of self-healing properties in materials is to prevent damage and even failure during service, failure is finally the result of an accumulation of nanoscale defects that can ultimately lead to rupture by crack propagation. Because early stages of damage occur at the nano- and microscale level long before failure, the most effective and useful healing methods address the early, small-scale events, and quantification methods are required that allow further insight at this level. In this respect, the different degrees of heat transfer in microscopic and macroscopic cracks is an important parameter in the healing process, and in consequence, the observation obtained from the healing process, an artificial macroscopic damage, is of limited use for the simulation of microcracks that materials will experience in real applications (Darabi et al., 2012).

One of the major requirements for the effectiveness of a self-healing efficiency quantification method is thus to successfully mimic the service conditions in the way that the conditions are simplified and standardized to the most possible extend, but not beyond. Only under this precaution it is possible to find the optimal formulation for a specific application. Without a fundamental understanding of the micromechanics and microstructural modifications, the development of commercial products will be compromised.

To evaluate self-healing in a way that at the same time can mimic real scale applications and ensures reproducibility, it is recommended the process to be divided in different steps. Figure 15 summarizes the different possibilities depending on the type of material and testing conditions. To evaluate self-healing efficiency it is necessary to establish a reliable and reproducible method for healing. Several factors need to be consider after establishing the testing setup, leading to different testing paths, as shown in Figure 15:

- The type of damage/repair cycle: the material exhibit cyclic healing or only a single event repair in-situ.
    - With some polymers, cyclic healing can be achieved even when the damage is applied in the same spot a second time.
    - In concrete the damage can only be repaired in a specific site once. After the new products, resultant from the healing reaction fill the crack, healing in the site is no longer possible.
- The initial conditions of the specimen.
    - Using a pre-notch, the crack propagation can be easily controlled for example, in brittle materials.
    - For some polymers and composites, a careful selection of the sample geometry is enough to ensure a reproducible damage. In this case no pre-notch is applied.
- The structural conditions for the control specimen
    - When the healing agent is encapsulated, the introduction of the capsules can either increase or reduce the material performance. In this situation the virgin sample should include the same type of capsules without healing agent.
    - The same logic applies to hollow tubes or microvascular systems, for example.
- The testing environmental conditions
    - Because MAX phase ceramics only exhibit self-healing in high temperatures, the tests need to be performed using real service conditions. This should ideally, include the whole process, from the initial crack until the test of the healed sample.

Independently of the particular property tested (e.g. compression, fatigue, ballistic impact, fracture, tensile strength), and of the corresponding analytical process, it is useful to establish a common definition of the self-healing efficiency. This facilitates the discussion and serves as a comparative basis among different materials. A suitable, generic definition relies on a normalization basis and the correct boundary conditions.

For a certain property *P* of a specific material, an optimal self-healing mechanism and process is characterized by the full restauration of the respective material property after a suitable, normalized damaging process. On the other side of the scale is a material that after healing still shows the property of the damaged sample. The healing efficiency η_i (*P*) with respect to *P* can be considered a function performance of a virgin sample (P_virgin), the damaged (P_damaged) and healed material (P_healed), and is meaningfully expressed as their ratio:

$$\eta_i(P) = \frac{P_{virgin} - P_{damaged}}{P_{virgin} - P_{damaged}} \qquad (5)$$

P_i is a certain property of the self-healing material. For a material where 3 different properties are to be assessed to evaluate its self-healing capabilities, it should be determined 3 efficiencies given as $\eta_1(P_1)$, $\eta_2(P_2)$ and $\eta_3(P_3)$.

As a matter of fact, generally more than one materials property are subjected to loss in case of damage – e. g., the elongation-at-break goes down simultaneously with tensile strength for longitudinal stress. The optimal quantification process thus enables to take into account more than one property in a suitable way. The overall efficiency is then a result of the combined efficiencies for the material subject to study and can be determined as an average of the efficiency obtained for each property (P_i).

Combining different properties into an overall efficiency helps to establish a common method to determine self-healing for distinct materials, using different testing methodologies. This opens the path to a common standard definition of self-healing independent of the testing method and material group.

The final average efficiency $\bar{\eta}$ based on a number n of properties for a self-healing material is accordingly determined as the harmonic mean given by equation 6 (Dodge, 2008).

$$\bar{\eta} = \frac{n}{\sum_{i=1}^{n}\left(\frac{1}{\eta_i(P)}\right)} = \frac{n}{\sum_{i=1}^{n}\left[\frac{1}{\left(\frac{P_{ihealed} - P_{idamaged}}{P_{ivirgin} - P_{idamaged}}\right)}\right]} \qquad (6)$$

When comparing efficiency values obtained from different properties for the same material, the traditional arithmetic mean is not suitable. The harmonic mean will be more appropriate, as it less sensitive to large outliers. When, for example, one of the efficiency values for the material is higher than 100%, while all the others fall below 70%, the highest result will influence less the harmonic mean, compared with the arithmetic one. When developing self-healing materials for industry, one must be cautious with very high efficiencies. They could give false information regarding the reliability of the material and its ability to self-heal. In real life applications this can raise safety and structural concerns.

7. Conclusion

The fast and encouraging progress that is achieved in the understanding and development of self-healing polymers, fibre reinforced polymers, coatings, ceramics and concrete as the most important material classes deserves the establishment of novel quantification strategies to facilitate the interdisciplinary discussion and the identification of generic principles. A comprehensive overview on the different healing and quantification methods currently employed for the different material classes helps in the identification of the basic concepts across the material classes. Even if most studies on self-healing materials are focusing on the mechanical performance and lifetime of a specific formulation, a broad variety of properties are of potential interest to be either fully or partially restored in a self-healing process, extending to optical, haptic, (thermal or electrical) transport, or barrier properties. As a general outcome, the importance of length and time scales as well as the relation to the actual service conditions is emphasized.

In addition, to select the appropriate assessment method for the quantification of the self-healing properties, the nature and the extension of the actual or expected damage needs to be taken into consideration in the first place.

An ideal quantification approach needs to take into account as well macroscopic as well as microscale aspects of damaging and healing. Depending on whether the experimental study aims at fundamental mechanistic insight, or on process or formulation optimization for proper functioning at the service conditions, the suitable and reproducible experimental environment, damage mechanism, and healing process needs to be identified. In view of potential applications, the ideal property recovery occurs at an early damage stage, and addresses a continuous repair of microcracks during operation. Nevertheless, the majority of present studies on self-healing materials still focuses on macroscopically applied damage such as scalpel cuts – even if this damage mechanism is far from the actual conditions in applications, it holds the advantage of easier standardization and thus facilitates the comparison across similar materials.

For an effective assessment of healed and original materials, it is important to choose the right mode that mimics the service conditions best. In this respect, mode I mechanical tests are similar to the mechanism of microcrack propagation, while mode III tests show problems concerning the inconsistency of the crack path. Several different geometries have been used. They include the width-tapered double cantilever beam (WTDCB), double-cantilever beam (DCB), tapered double-cantilever beam (TDCB), compact tension (CT) and the single-edge notch beam (SENB). In DCB, WTDCB and TDCB samples it is possible to obtain a controlled crack growth along the centre. Crack length is then independent from fracture toughness depending only on the applied load. CT specimens are influenced by the clamping pressure, requiring a careful control of the pressure to ensure reproducible results.

Another important issue that needs to addressed and carefully documented to result in a reproducible and useful quantification process is the nature and age of the contact areas. The best mechanistic insight can be expected when the quantification process allows to be separated according to the different stages of self-healing.

The self-healing ability of a given material is often referred to as the ability to recover a specific property relative to the virgin or undamaged specimen. In polymers, repairing is assessed by mechanical restoration of different properties, in fibre-reinforced polymers is usually assessed by comparing fracture toughness and strength, before and after repairing.

When looking at industrial applications for self-healing materials one critical aspect is the long-term ability to restore strength. Research in this field has been focused in damage repair and there is a need for further studies regarding cyclic healing and fatigue damage. Some researchers have done important advances in modelling and predicting self-healing behaviour however, this needs to be complemented with further experimental work.

The ability to self-heal is generally defined as a healing efficiency η given on a percent scale. In a suitable and generic definition of the self-healing efficiency with respect to a certain property and damage mechanism, the performance of not only the virgin and the healed material need to be taken into account, but also that of the accordingly damaged, non-healed material. In addition, the proposed set of definitions holds the potential to consider more than one relevant property to be compared directly by addressing a spectrum of properties.

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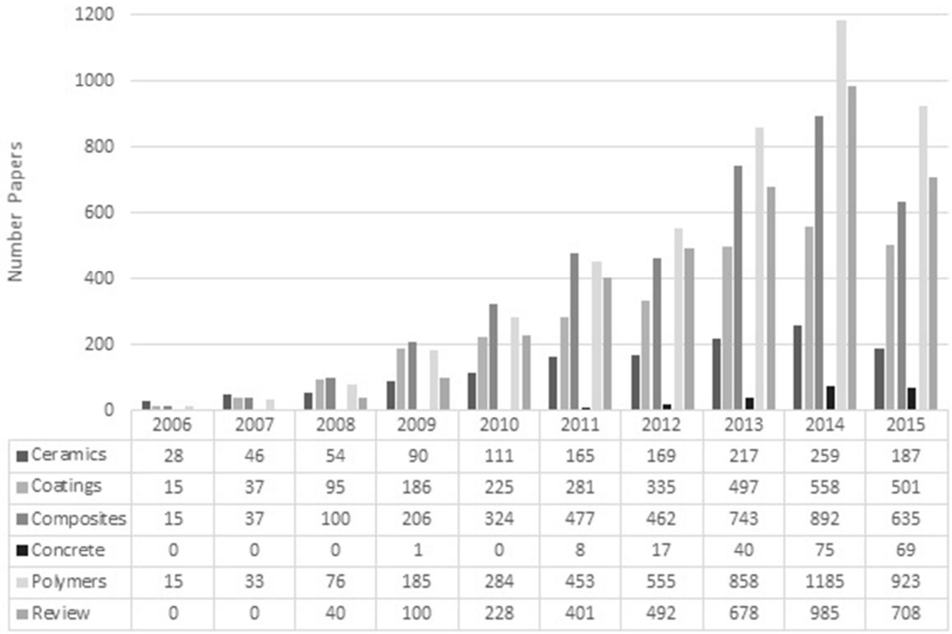
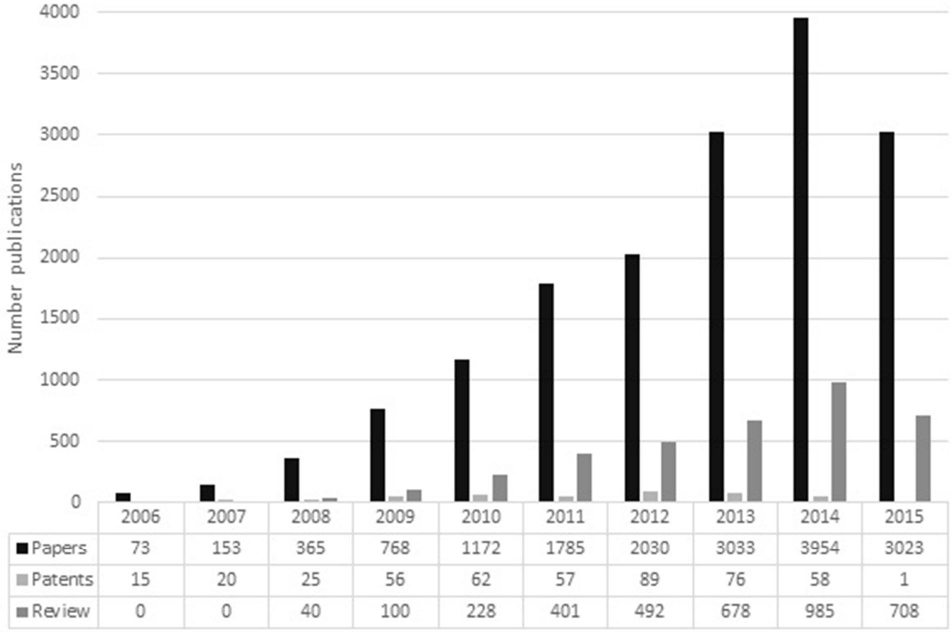
Materials	Damage mechanism	Healing
Polymer	Razor blade/scalpel cut Tensile test with rupture Ballistic impact Fracture toughness Shear test	Intrinsic healing Supramolecular networks
	Razor blade/scalpel cut	Temperature triggered Supramolecular networks
Polymeric coating	Microcutting with corrosion Corrosion/erosion Pull-out tests (adhesion) 3 or 4-point bending Microscratching	Molecular inter-diffusion (solvent) Encapsulated agent
Concrete	Controlled crack initiation by bending Compression	Activation of microencapsulated agent
Ceramic	Crack initiation by indentation Synchrotron mechanical test Tensile force Biaxial ball on three balls High temperature stress 3 or 4-point bending	Temperature triggered Oxidation reaction
Ceramic coating	Crack initiation by indentation High temperature stress 3 or 4-point bending	Temperature triggered Oxidation reaction
Composite	Crack induced rupture of fibres Fracture toughness Fatigue loading Delamination Impact by indentation 4-point bending Notched flexure	Healing agent released by microvascular networks



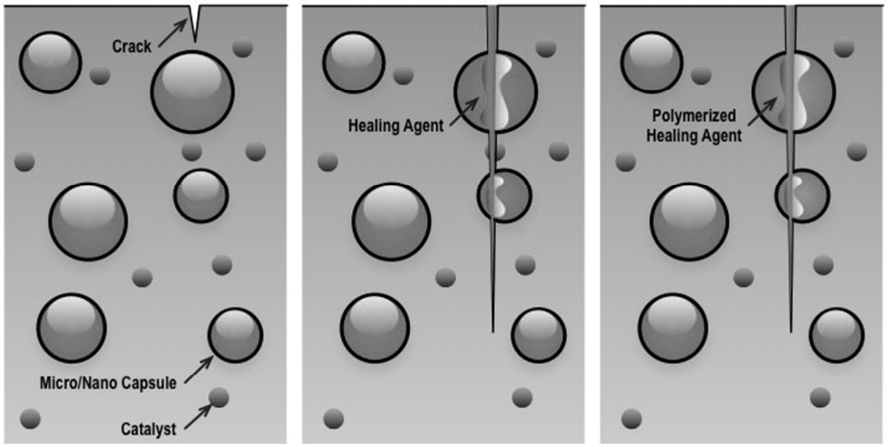
	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
■ Ceramics	28	46	54	90	111	165	169	217	259	187
■ Coatings	15	37	95	186	225	281	335	497	558	501
■ Composites	15	37	100	206	324	477	462	743	892	635
■ Concrete	0	0	0	1	0	8	17	40	75	69
■ Polymers	15	33	76	185	284	453	555	858	1185	923
■ Review	0	0	40	100	228	401	492	678	985	708

Publications in the field of different self-healing material classes in scientific journals since 2006 (source: ISI Web of knowledge)
128x83mm (120 x 120 DPI)

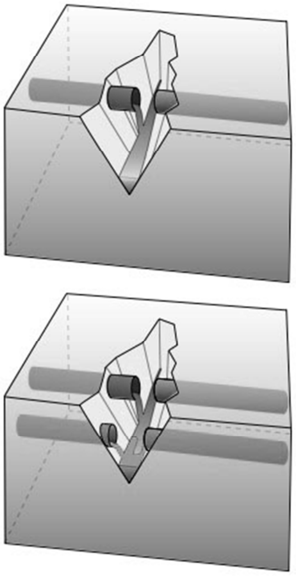


	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
■ Papers	73	153	365	768	1172	1785	2030	3033	3954	3023
■ Patents	15	20	25	56	62	57	89	76	58	1
■ Review	0	0	40	100	228	401	492	678	985	708

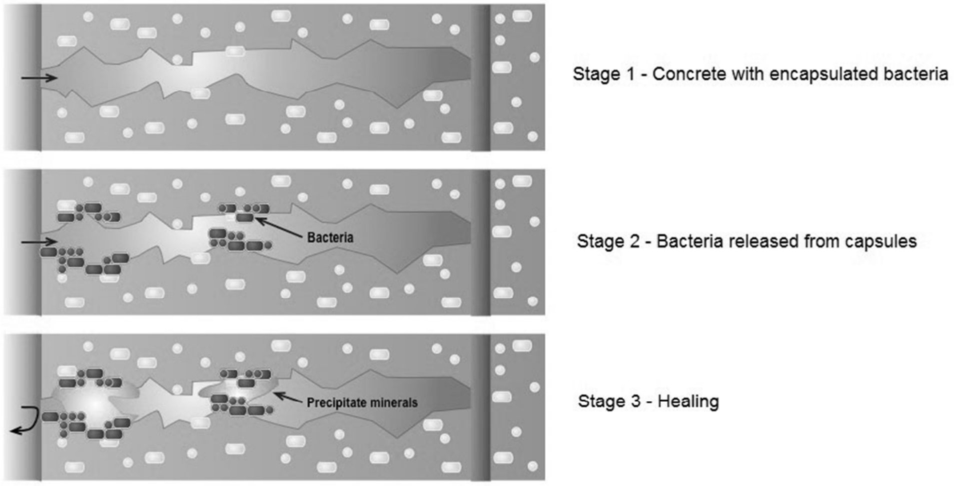
Scientific publications and patents on self-healing materials issued since 2006 (source: ISI Web of knowledge)
128x83mm (120 x 120 DPI)



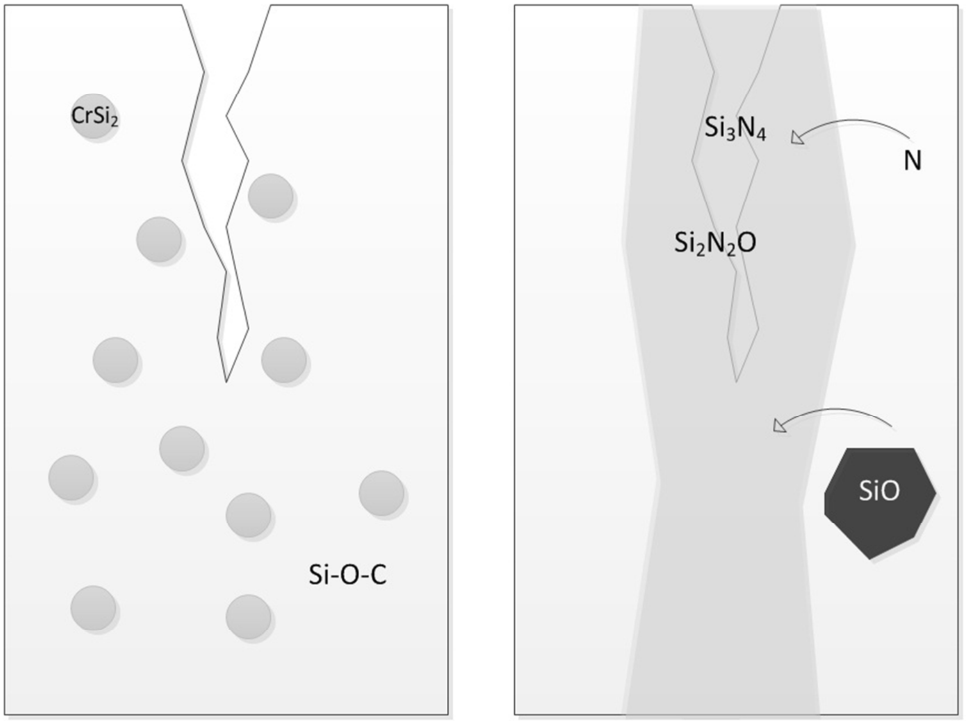
Polymer self-healing by agent encapsulation and release upon damage
283x189mm (72 x 72 DPI)



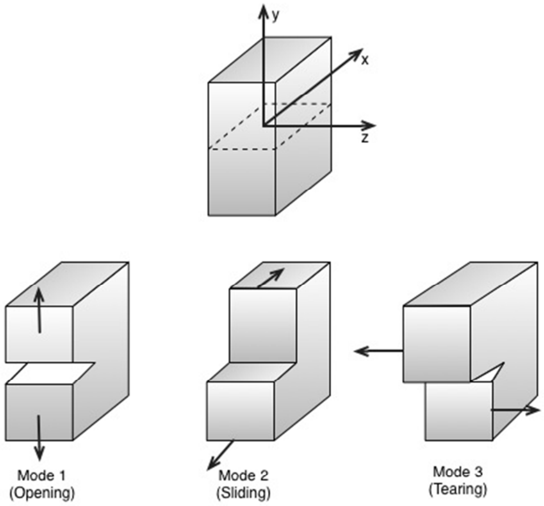
Self-healing in composites containing a microvascular network with reactive fillings. a) one-component system, b) two-component system.
283x189mm (72 x 72 DPI)



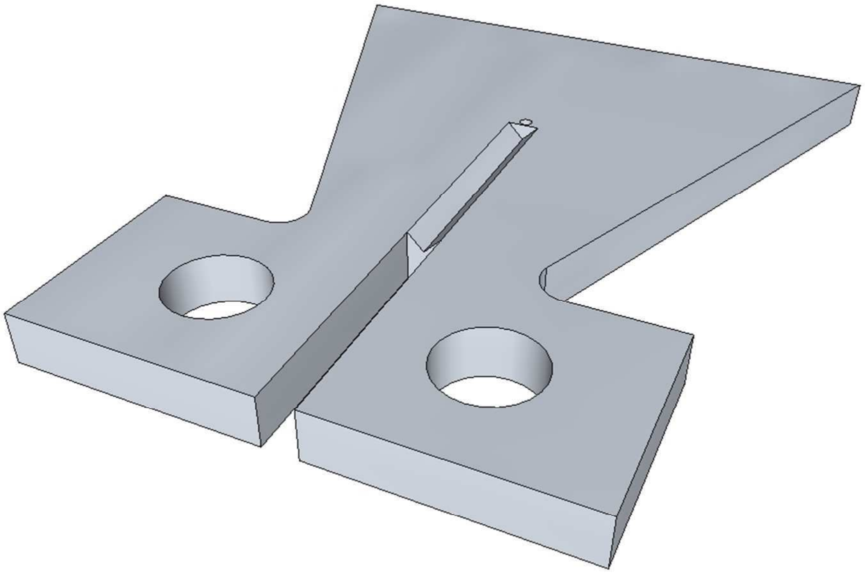
Bacteria-based self-healing in concrete.
345x178mm (72 x 72 DPI)



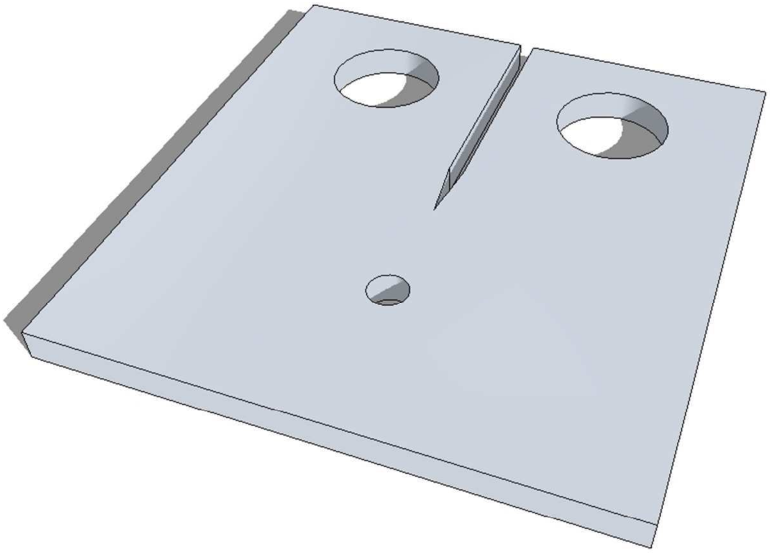
Self-healing of a microcrack in a Si-O-C ceramic oxide by diffusion/oxidation.
238x178mm (96 x 96 DPI)



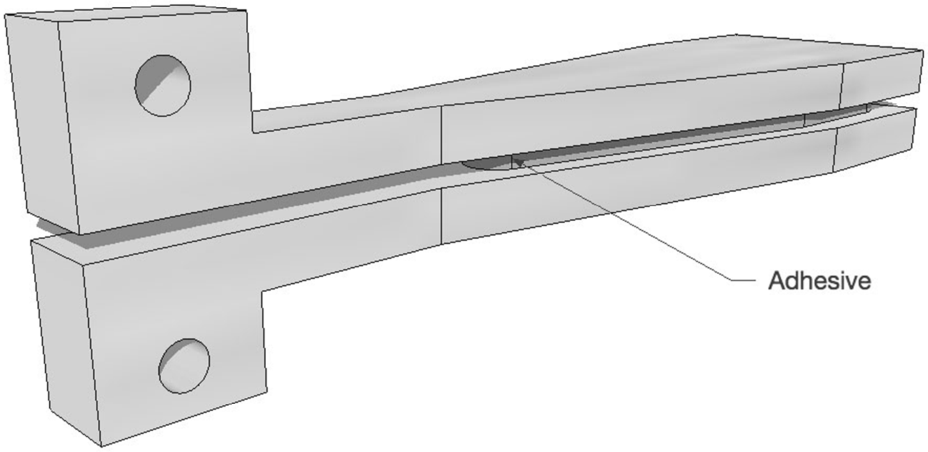
Fracture testing modes.
283x189mm (72 x 72 DPI)



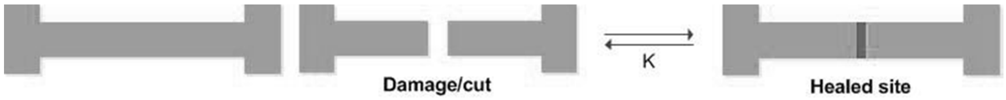
Tapered double cantilever beam (TDCB) sample geometry for the mode 1 quantification of the mechanical self-healing ability of structural materials.



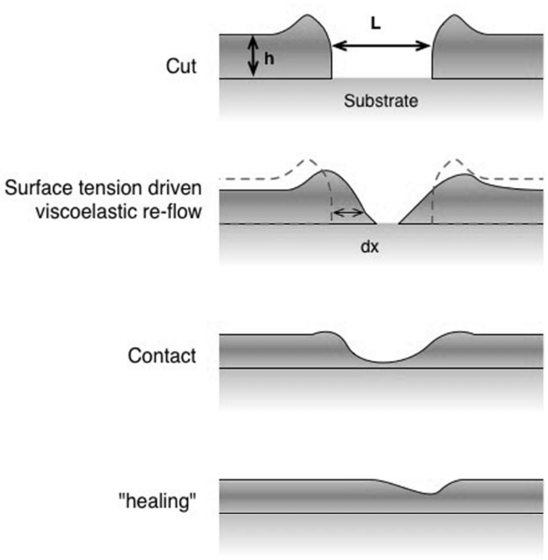
Compact tension (CT) sample geometry for self-healing ability quantification.



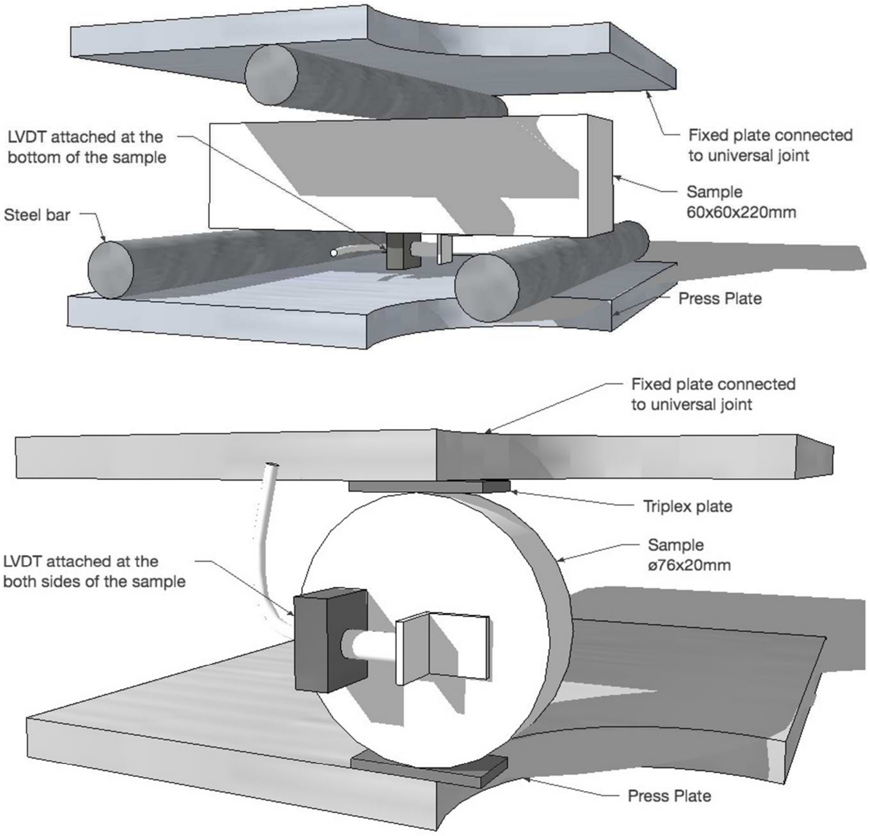
Width tapered double cantilever beam (WTDCB) sample geometry for self-healing ability quantification.
336x232mm (72 x 72 DPI)



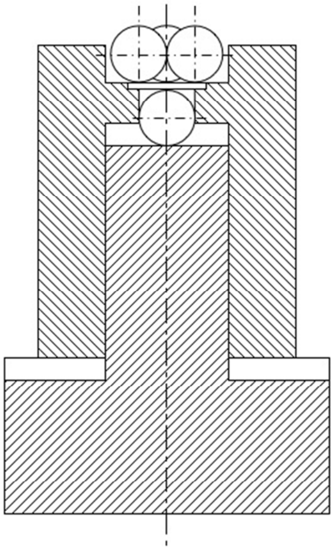
Healing trough a razor blade cut.
202x19mm (96 x 96 DPI)



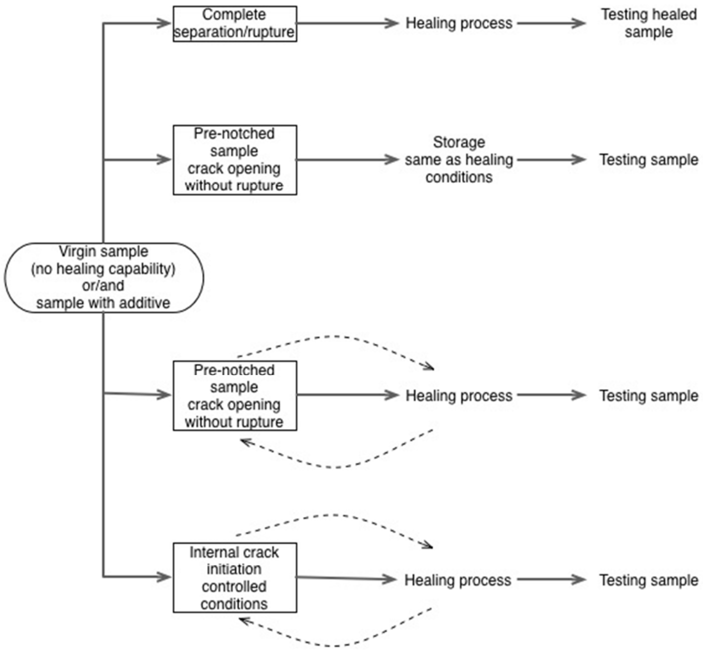
Healing mechanism in coatings.
283x189mm (72 x 72 DPI)



3-point bending test in concrete.
229x204mm (120 x 120 DPI)



Biaxial ball-on-three balls (B3B) test.
283x189mm (72 x 72 DPI)



Standardized routes for testing self-healing materials.
283x189mm (72 x 72 DPI)