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Огляд

Self-healing polymers: approaches of healing and their application

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Self-healing (S-H) polymers are a new class of smart materials with extended lifetimes that have the capability to repair themselves when they are damaged without the need for detection or repair by manual intervention of any kind. This paper reviews briefly the studies devoted to the development and characterization of S-H polymeric materials. All relevant approaches in preparation of such polymers can be divided into two groups: autonomic and non-autonomic. Autonomic healing are fully self-contained and requiring no external intervention of any kind, however this method of self-healing is also known as extrinsic because of presence of additional healing agent placed in reservoir in polymer material. Autonomic healing can be further divided into sub-categories based on the self-healing concept employed. The subcategories include: capsule systems and microvascular or fiber network-based systems. Non-autonomic healing are partially self-contained; healing capability is designed into the material, that is why this method is also named as intrinsic. But additional external stimuli such as heat or UV-radiation is required for the healing to occur in this method. Intrinsic self-healing polymer can be tailored to become chemically 'sticky' along break lines. Polymers can also be designed to respond to a variety of different energetic conditions, e.g. specific electromagnetic fields or bullet permeation. This paper also examines critically benefits and shortcomings of each example of approaches proposed to prepare the S-H systems. Emerging self-healing technologies designed to give polymeric materials the capability to arrest crack propagation at an early stage thereby preventing catastrophic failures will go a long way in helping to increase the scope of applications of these materials. Such techniques are very useful for repairing damage to satellites and spacecraft caused by high-speed debris. Another attractive range of application of S-H polymers observed in this review includes S-H coatings and adhesives. Finally, the challenges and research opportunities are highlighted.

Key words: smart materials, self-healing polymers, polymer composites, adhesives, coatings.

Polymers and polymer composites have been widely used in tremendous engineering fields because of their advantages including light weight, good processibility, chemical stability in any atmospheric conditions, etc. However, long-term durability and reliability of polymeric materials are still problematic when they serve for structural application [1]. Exposure to harsh environment would easily lead to degradations of polymeric components. Comparatively, micro cracking is one of the fatal deteriorations generated in service, which would bring about catastrophic failure of the materials and hence significantly shorten lifetimes of the structures. Since the damages deep inside materials are difficult to be perceived and to repair in particular, the materials had better to have the ability of self-healing [2].

On the whole, researches in this field are still in the infancy. More and more scientists and companies are interested in different aspects of the topic. Innovative measures and new knowledge of the related mechanisms are

constantly appearing.

Self-healing approaches.

Mending, self-healing (S-H) of polymer and related composites were always on the top of the wish list of researchers. Many concepts have been introduced for the healing of bulk polymers and their feasibility checked [3]. A polymer displaying self-healing properties needs the ability to transform physical energy into a chemical and/or physical response able to heal the damage – a process which normally is not present in “conventional – non-self-healing” polymers [4]. The related approaches are differently classified. Classifying usually considers whether or not the healing requires an external stimulus. When no external stimulus is required and healing agent has to be preembedded then mending is termed as to **autonomic**, whereas its triggering with additional treatment when polymers are able to heal cracks by themselves (usually heat) is called to **non-autonomic** [5]. Note that in both cases the healing agents are available in the bulk material

though in very different forms. Healing agents may be in reservoirs (capsules, capillaries) which break up upon external mechanical damage thereby initiating the healing reaction. When a catalyst is required, then it may be incorporated in the matrix polymer, available in one of the healing components in non-active or latent form, and the like. The chemical build up of the healing agent may markedly differ from that of the matrix [6].

There are many papers in the literature related to the self-healing materials [7]. They show that there is another classification of self-healing methods based on the property of material. This classification divides all methods into **intrinsic** and **extrinsic** ones. The **intrinsic** self-healing composites the predominant molecular mechanisms involved in the healing processes can be due to physical interactions, and/or chemical interactions (for instance thermally reversible reactions, hydrogen bonding, ionic coupling, a dispersed melttable thermoplastic phase, molecular diffusion, etc.). In the case of **extrinsic** self-healing composites, a healing agent has to be stored in vessels and embedded into the polymeric matrix in advance during the manufacture of the material. This capsule-based method was developed by White and co-workers [8–11]. As the cracks destroy the fragile vessels in which the healing agent is stored, this would be released into the crack planes, due to capillary forces, and heal the cracks. In accordance with the types of containers these materials can be classified into different groups, among which are: self-healing in terms of healant-loaded **pipelines** [7], self-healing in terms of healant-loaded **microcapsules** [7, 12], and self-healing in terms of **vascular** materials [13–20] in which the healing agent is sequestered in a network in the form of capillaries or hollow channels [3, 21–25]. These chemical binder-based methods change the material composition at the damage site during healing and hence can be used to heal a damaged site in this material only once.

Intrinsic type of healing is used to heal, for example, thermoplastics by molecular re-entanglement processes. As was mentioned, re-entanglements across the (broken) surfaces of thermoplastics are typically triggered by heat. The temperature, at least locally, should be higher than the glass (T_g) or melting temperature (T_m) depending whether the actual polymer is of amorphous or semicrystalline nature. This is also the basic principle of thermoplastics welding. This means that an important aspect of intrinsic self-healing is the presence of a structure which is able to dynamically respond to an external stimulus [26], enabling the restoration of the initial material properties. Due to their highly complex chain structure, polymers, in particular, are ideally suited to serve as molecules for dynamic and thus self-healing properties. Thus, the polymers are coupled to fast and efficient cross-linking reactions [27].

A five-stage mechanism to unscramble the complexity of strength recovery at ruptured polymer/polymer

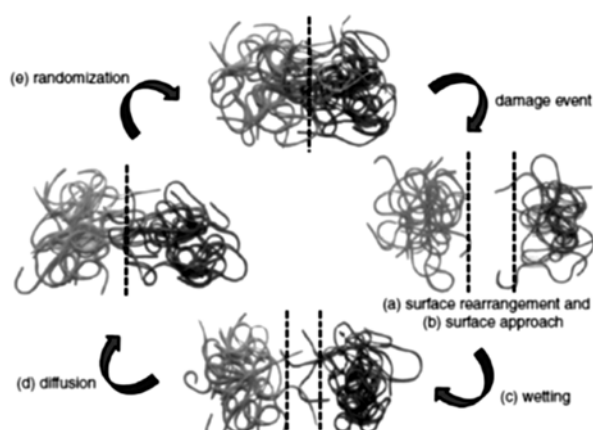


Fig. 1. Stages of self-healing mechanism: surface rearrangement (a); surface approach (b); wetting (c); diffusion (d); randomization (e) [4]

interfaces, and provide an explanation for the functioning principle of many self-healing concepts (Fig. 1), being strongly related to *molecular interdiffusion* at or above the T_g has been suggested [28]. At this temperature polymer segments are mobile enough to enable an efficient self-healing process. This relatively simple model is, in its basic steps, applicable as a universal mechanism for nearly all self-healing concepts [29].

Healing by re-entanglement in amorphous polymers was already performed in the 1980s, pioneered by the group of Kausch [30, 31]. Interestingly, already at this time fracture mechanical treatise was used to quantify the healing efficiency, which remained the dominant tool until now [32]. Both amorphous and semicrystalline thermoplastics are often used for the toughening of thermosetting resins. The resulting morphology may be very different. Considering just the amount of the modifier the morphology is varying between different dispersed and continuous structures. It is the right place to mention that a co-continuous morphology composed of thermoplastic and thermoset phases, is termed to as semi-interpenetrating polymer networks (semi-IPNs). The preferred morphology for the purpose of toughening was micron-scale dispersion of the thermoplastic phase in the thermosetting matrix [33]. This is usually achieved with a thermoplastic content of less than 15 wt.%. It is intuitive that this thermoplastic phase, in whatever morphology present, may work for healing. One would expect that a semi-IPN structure results in a better healing than a dispersed morphology [34–36].

This requirement can be easily met by poly(ϵ -caprolactone) (PCL) having a melting temperature of about 60 °C [37]. Moreover, PCL is a polyester that should have good solubility in epoxy resin (EP). It is available commercially in different molecular weights which is a further tool to control its dissolution in EP. In fact, PCL has been tried as toughening agent in EPs from the 2000s [38]. Attempts were also made to control its reaction-induced phase separation through further additives, such as organo clay

[39]. Thermal mending of EP via thermoplastic PCL was first explored by Luo et al. [40]. The cited authors modified an aromatic amine-cured diglycidyl ether of bisphenol A-based EP (DGEBA) with PCL, added up to 34.9 wt.%. They revealed that the morphology above 15.5 wt.% PCL content consisted of a continuous PCL phase in which interconnected EP spheres are dispersed. As a consequence, the PCL phase may serve for thermal mending of this high T_g EP that was proven, in fact.

Another work was devoted to studying the thermally induced healing via reentanglement of molecules of the thermoplastic PCL phase formed by phase separation in EP resins upon their curing [5]. PCL was dissolved in various amounts in EPs initially exhibiting higher [EP(H)] and lower T_g values [EP(L)] than the T_m of PCL. Healing was triggered at 80 °C which was at about to far beyond the above transition temperatures. Note that the T_g of the EPs varied with the EP/PCL compositions. Based on this study, it can be concluded, that the development of a bicontinuous, semi-IPN-like structure in EP/PCL strongly contributes to the thermally induced healing, also when performed repeatedly.

Thermal methods to heal a damage have been investigated for structural polymers (mendable polymers or “mendomers”) [41–43]. The heat required for healing in mendomers is provided by a processes extrinsic to the material and at a time chosen by the damage detection method. In another thermal method, Kalista [44] uses an **ionomeric polymer** (Surlyn) to demonstrate autonomous self-healing. In this work, *heat generated during the damage event such as ballistic impact is harnessed to melt the polymer at the damage location to heal the damage* [45–48]. Smart Materials Research by Kalista [45], Kalista and Ward [46], and Varley and Vander Zwaag [47] demonstrates an interesting concept, it does not apply to damage occurring in a material curing regular wear and tear. To advance the use of Surlyn in self-healing, Owen [49] developed a novel approach to mitigate this deficiency with Surlyn by dispersing magnetic particles in Surlyn. This method, while taking a step in the right direction, requires a large induction coil to heal the damage in the sample. In addition to these methods, self-healing methods presented in the review paper by Wu et al. [50], self-healing sensor skin [51], bioinspired methods developed by Trask et al. [13, 52], and recent work by White group [53] demonstrate novel techniques for healing structural damages. Alongside these works, there has been a renewed interest in thermoplastic polymers that use **reversible ionic aggregation to function as self-healing materials** [54–55].

The current state-of-the-art in self-healing, with the exception of some thermal and photochemical methods, requires chemical modification to the structure and cannot be healed at a damage site after one damage event. While photochemical self-healing has proved to be able to induce repeated healing of damages at the same damage site, it lacks the structural capabilities of a desired

self-healing composite. It is evident that a chemical binder, once consumed, cannot be regenerated after the healing process is complete. In addition, the chemical binder-based methods that use microcapsules and vascular networks for healing a damage require a minimum volume of the binder filled in the hollow cavity to heal the material. The microcapsules or vascular networks are practically obtrusive for use *in thin polymer films* such as wire-insulation material in aerospace applications. So there is a need to develop a self-healing technique for thin membranes that can be repeatedly healed by the application of heat. It is anticipated that this composite material will be useful as one of the layers of a wire-insulation composite, inflatable membranes, and aerodynamic surfaces of microair-vehicles and in various aerospace applications. **The aerospace application of self-healing materials.**

One of the biggest challenge facing materials scientists is the idea to put in action self-healing composites in aeronautic or in general aerospace applications. Epoxy resins are fast gaining ground as the preferred polymer to be used as carbon fiber-reinforced materials to manufacture large components being able to sustain aerodynamic loads. The introduction of these resins to the aeronautic industry was mainly driven by performance gains (better design flexibility, no corrosion, easy production process, etc.) and most of all by weight reduction. This last aspect is of relevance when considering issues related to the energy resources and supply, costs in service and air pollution measures. This major advantage of the composites, the lightness, is also obtained by saving and/or increasing the material strength in such a way as to make traveling on aeroplanes more comfortable for the crew and passengers in virtue of the possibility to slightly increase cabin pressures without increasing the structure weight. Unfortunately, composites also possess some properties which reduce their advantage with respect to traditional metal alloys. One inherent shortcoming is the poor impact damage resistance. Impact damage can be due to several factors, such as unfavorable weather conditions, stones or rocks on the keel during landing, incidental contact during maintenance, and bird strike. It may significantly affect the integrity of the composite structure of aircraft in service [56]. This process starts at the microscopic level with the formation of micro voids which then expand to generate deep micro cracks within the structure [57]. Impact damage may lead to substantial matrix micro cracking and delamination within the bulk of the composite, reducing the structural capability and leading to premature failure, if it is not detected and repaired. Damage can also provide a route for the ingress of contaminants into the structure [57]. The internal damage is difficult to detect and even more difficult to repair and, once it has developed, the integrity of the structure is greatly compromised. Restoration of the physico-mechanical properties of such a material, once fractured, requires either new covalent chemistry to generate additional cross-links,

or long periods of an healing to enable thermal diffusion of unbroken, linear polymer chains into the damage zone [58]. Several non-destructive damage detection techniques have been developed, including ultrasonics, infrared thermography, X-ray tomography, and computerized vibro-thermography. This technology can help with damage detection, but generally the repair entails strong increases in the aircraft operating costs and, in addition, sometimes the damage is not visible from outside. Furthermore, in a composite, the weave is characterized by different directions in different parts, so repairing structural parts is very difficult. Many times the current technology related to the repair methods, such as welding or patching, can be applied at the macroscopic level to either rejoin or reinforce damaged areas. However, these solutions are not always useful, either as a result of inaccessibility to the damaged area, or because they lead to changes in the strength of the material, producing inter-phase surfaces that can act as weak regions of lower mechanical performance. It has been shown, in fact, that the *location of the weld remains the weakest point in the material*, and thus the site for future damage to occur. An aircraft with inherent self-healing and/or protective abilities could help to significantly extend the inspection intervals, thereby increasing aircraft availability. Alternatively, existing inspection intervals could be maintained with significantly thinner structures, thereby *saving airframe weight* and hence *reducing fuel burn*, in-service cost, and the environmental impact. Recent studies have highlighted the potential of self-healing polymer composites to be used as single structural materials, and/or for sandwich structures. The main difficulty in the development of these smart materials is due to the nature of the composite used as structural materials. In fact, the self-repair activity has to be highly efficient in a relatively rigid structure (with reduced mobility of the molecular segments). In addition, most of the functionalities responsible for triggering self-repair actions have to be active after the drastic conditions of curing cycles used in the field of aeronautic materials. In fact, the *high temperatures required in the curing process deactivate many of the already available self-repairing reactions*.

As was mentioned above, according to the ways of healing, polymer composites can be classified into two categories: intrinsic ones and extrinsic. For structural applications such as aeronautic materials, the *extrinsic* self-healing systems are of great interest because they would overcome the difficulties connected with damage diagnosis, and allow the following appropriate interventions to be reduced. The first capsule-based self-healing system for thermosetting materials was proposed by the team from the University of Illinois [12]. The concept was based on the introduction of a micro-encapsulated healing agent and a suspended catalyst phase in an epoxy matrix. Since that time, advances have been made in the field following this conceptual approach and, although alternative

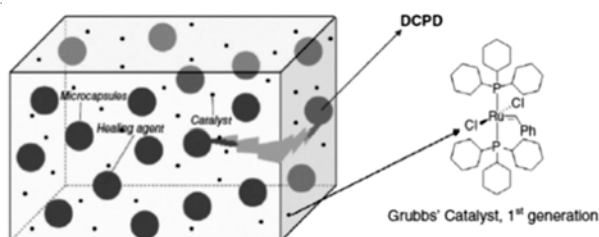


Fig. 2. Design of the first self-healing system relying on capsule-based concepts [12]

concepts have emerged in the scientific literature, for many systems a similar healing mechanism based on the ring-opening metathesis polymerization (ROMP) of the healing agent was proposed [3, 59–71].

Among the systems relying on capsule-based concepts, the initial self-healing epoxy system involves the incorporation of a microencapsulated healing agent, dicyclopentadiene (DCPD) and a dispersed solid catalyst, bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (called Grubbs' catalyst) in an epoxy-amine network [12] (Fig. 2).

The *reaction that allows repair of a mechanically induced damage is based on the polymerization of the healing agent released through capillary action that is triggered by contact with the embedded catalyst, bonding the crack faces within the polymeric matrix*. The efficiency of the self-repair function, in terms of trigger, speed and yield, is related to ROMP of the healing agent by **appropriate catalysts**. The healing agent is a microencapsulated liquid monomer that must have a long shelf life, prompt deliverability, high reactivity, and low volume shrinkage upon polymerization [60]. The monomer most often used as the healing agent for the manufacture of these first ingenious systems is DCPD [3, 60]. Moreover, blends of DCPD/5-ethylidene-2-norbornene (DCPD/ENB) or DCPD/5-norbornene-2-carboxylic acid have also been proposed [72]. Thermosetting auto-repair polymers, which have been proposed so far, include Grubbs' first-generation catalyst (G1) [3, 73–76]; and currently, the possibility of applying other ruthenium catalysts, such as second-generation Grubbs' catalyst (G2) and Hoveyda–Grubbs' second generation catalyst (HG2), is under evaluation [73, 77, 78]. However, this system has some drawbacks. The first one is the *thermal stability* of the ruthenium catalysts inside the epoxy resin during the curing cycle [73, 78], and the second is the *impossibility of utilizing primary amines as hardeners*, since they can **poison the catalyst**. At the high temperatures of the curing cycles scheduled for epoxy formulations, *thermolytic decomposition can limit the usefulness of these ruthenium systems* in self-healing composites based on epoxy resins. This is a crucial aspect for self-healing systems in aeronautic applications because, even if linked to the cost reduction from a process aspect, resins have been developed with *low temperature manufacturing* (under 100 °C), yet the

problem of the material treatment at high temperature is currently under investigation. For aeronautic applications, it is also critical that *the self-healing activity functions at low working temperatures*, which can reach values as low as 50 °C. This issue is even harder to solve for space vehicles or satellites where extreme fluctuations of temperature *between -150 and +150 °C* are also possible. Indeed, a very efficient aeronautic or aerospace self-healing material needs to satisfy these two fundamental requirements: (i) **chemical stability and high thermal stability of the self-healing components** (catalysts and vessels filled with healing agents), (ii) **high healing efficiency at low temperature**.

Stability and Reactivity of Catalysts for Self-Healing Formulations. Wilson and coworkers have evaluated the reactivities of G1, G2 and HG2 catalysts with various monomeric healing agents with a view toward improving the self-healing performances in a variety of epoxy matrices [73]. In the same paper they have also evaluated the thermal stability of these three catalysts embedded into the epoxy matrices with the aim of studying their stability to processing conditions during manufacturing conditions.

Self-activated M1 samples (epoxy matrix EPON 828 cured with DETA) containing 1.5 wt.% of as-received catalyst were prepared and subjected to customary curing cycles [3, 61, 64, 67] followed by an additional post curing at 125 °C for 4 h before fracture testing. This fracture test showed that the lower retention of healing performance observed for HG2 catalyst was an unexpected result since HG2 is a catalyst with impressive chemical stability and recyclability [73, 79, 80], great functional group tolerance, as well as greatly enhanced air and water stability [81]. In a recent paper [78] Guadagno and coworker have shown critical issues in the use of epoxy precursors in conjunction with HG2 metathesis catalyst. However, an appropriate curing cycle of the self-healing mixture allows to carry out the curing process at high temperatures without deactivating the self-repair activity. The HG2 catalyst showed exceptional stability, even after a thermal treatment at 180 °C in air atmosphere.

Using FTIR spectroscopy to monitor the reactivity of the epoxy groups [82], the authors demonstrated the reactivity, at temperatures higher than 80 °C, of the HG2 catalyst embedded inside the epoxy matrix with the oxirane rings and found compromised effectiveness in the activation of the ROMP. The same authors found a solution to preserve the catalytic activity of HG2 catalyst inside the epoxy matrix. The addition of a step in the curing cycle, at a temperature at which the HG2 catalyst does not react in competition with the hardener (below 80 °C) allows the opening of all the oxirane rings, preserving its catalytic activity in successive curing steps at higher temperatures. In this way, the catalyst remains intact, and hence it is capable of subsequently performing its catalytic activity in the ROMP of healing agents. This stratagem allowed the obtaining of samples cured at temperatures

up to 160 °C without deactivating the self-repair activity of the formulated systems. Curing cycles currently used in the aeronautic field for primary structures may reach temperatures up to 180 °C. Concerning this last requirement, recent works have shown very promising results when the self-healing formulation contains Hoveyda-Grubbs' 1st generation catalyst rather than G1, G2 or HG2 catalysts [83-87]. The thermal stability of each of the catalysts G1, G2, and HG1 was evaluated under conditions of actual use for applications in self-healing structural systems. The catalyst was dispersed in the epoxy matrix in its solid state and both the epoxy precursor and the composite were cured by two-stage curing cycle; after which, the catalysts were extracted with chloroform from the epoxy matrix (after the curing process at high temperatures) and analyzed by ¹H-NMR spectroscopy. It is observable that Grubbs' 1st generation and 2nd generation catalysts are stable if the temperature of the second stage of the curing cycle is up to 150 °C for 2 h; it is not possible to formulate self-healing systems related to ROMP of the healing agents when a curing temperature of 180 °C is scheduled. Epoxy self-healing systems containing HG1 can be processed even with a temperature of the second stage up to 180 °C.

Another issue related to the stability of self-healing components is the *instability of the catalysts* embedded in epoxy formulations *to primary amines*, which represent an important class of curing agents for epoxy formulations. In order to formulate a self-healing aeronautic resin, it should be taken into account that the final material must have *suitable mechanical properties* which depend not only on the curing cycles, but also on the chemical nature of the epoxy formulations. In the choice of epoxy mixture, it is necessary to consider that the *structure of the resin strongly governs its chemical and some of its physical properties*. This, combined with the nature of hardener agent, the functionality, the stoichiometry, and the curing cycle determines the final properties of the cured resin, especially in terms of mechanical and thermal properties. Generally, hardeners (curing agents) based on the primary amines give the best mechanical performance. Unfortunately, these amines can poison many of the catalysts active in ROMP of monomers used as healing agents. The instability of ruthenium catalysts to primary amines can be a significant drawback in the design of self-healing polymers; for this reason it is fundamental to evaluate the activity of the catalysts embedded inside the specific epoxy formulation [3, 61, 88].

Healing Efficiency at Low Temperatures. In aircraft, the operating range may vary roughly from -50 to +60 °C, therefore the healing agent must be able to heal the material also at very low temperatures. Merle and coworkers in a recent patent proposed the use of 5-ethylidene-2-norbornene (ENB) as a healing agent active at low temperature [89]. Guadagno et al. analyzed the ROMP of this healing agent using G1, G2 and HG1 catalysts. The obtained

Table. Reaction rate and yield of ROMP reaction of DCPD and ENB with G1, G2 and HG1 catalysts

Test	Catalyst/monomer ratio	Temperature, °C	Time, min	Yield, %
1	1:1000 G1/DCPD	25	15	34
2	1:1000 G1/DCPD	0	5	0
3	1:1000 G1/DCPD	10	30	0
1	1:1000 G1/ENB	25	0,5	100
2	1:1000 G1/ENB	0	13	100
3	1:1000 G1/ENB	-10	60	17
4	1:1000 G1/ENB	-20	1440	79
5	1:1000 G1/ENB	-30	1440	74
6	1:1000 G1/ENB	-40	1440	52
1	1:1000 G2/ENB	25	1	99
2	1:1000 G2/ENB	0	50	100
3	1:1000 G2/ENB	-20	60	79
4	1:1000 G2/ENB	-30	1440	74
5	1:1000 G2/ENB	-40	1440	43
1	1:1000 HG1/ENB	25	0,5	96
2	1:1000 HG1/ENB	-20	1440	93
3	1:1000 HG1/ENB	-40	1440	99
4	1:1000 HG1/ENB	-40	240	98
5	1:1000 HG1/ENB	-50	450	99

results were compared with those obtained using the most common healing agent (DCPD monomer) [84, 85, 90]. Table 1 summarizes data from all the performed experiments.

The self-healing functionality based on the metathesis reaction of DCPD activated by the G1 catalyst deactivates if the damage occurs at a temperature equal to or lower than 10 °C. On the other hand, the metathesis reaction activated by G1 and G2 catalysts with ENB is active even at -40 °C. A comparison with DCPD data highlights the advantages of ENB as healing agent. The yield reaches a value of 100% after a reaction time of 30 s at 25 °C, compared to DCPD where the reaction yield is about 34% after a reaction time of 15 min. In the case where HG1 is used as catalyst and ENB as healing agent, the metathesis reaction is significantly active also at -50 °C, whereas with G1 and G2 activity is reduced already at -40 °C. **The systems based on ENB as healing agent and HG1 as catalyst offer the most promising results. In fact, HG1 showed a higher thermal stability and optimal reactivity for ROMP at low temperatures.**

The healing efficiency η (calculated as the ratio between the critical fracture loads of the healed and virgin samples) was obtained from load–displacement curves using an already established procedure [91, 92]. The results are shown in Fig. 3. The healing efficiency was found to be about 91%.

The following work deserves special interest in the field of aerospace application. The attractive self-healing material presented in the Sundaresan with co-authors paper is a composite material prepared by embedding carbon fibers in Surlyn 8940 (referred to as “Surlyn” from this point forward) [93]. Surlyn is an ethylene/methacrylic

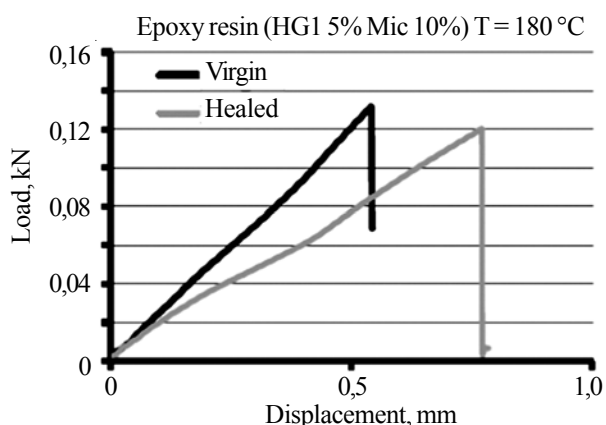


Fig. 3. Load–displacement curves for virgin and healed epoxy sample (HG1 5% Mic 10%) cured up to 180 °C [92, 93]

acid (E/MAA) copolymer in which the MAA groups are partially neutralized with sodium ions. This sodium ionomer is chosen as the matrix of the self-healing composite for its low melt temperature of 95 °C and previously demonstrated healing capabilities. Carbon fibers are selected as a heating element due to its low electrical resistance, resistive heating property, and reinforcement properties. Other properties, such as low density and high strength, make this an attractive option over other heating elements. Carbon fiber bundles in the self-healing composite demonstrated in this work are arranged in a unidirectional pattern between two layers of Surlyn sheets (200 μ m thick) and melt-pressed into a composite. For testing and characterization, two configurations of carbon fiber in Surlyn is fabricated for this work. In the first configuration, the carbon fibers are uniformly distributed in the matrix. In the second configuration, bundles of carbon fibers are distributed throughout the sample with finite spacing between adjacent bundles. Each bundle containing 1000 carbon fiber threads is used as a singular unit. The carbon fibers distributed in the composite are exposed at the two ends (or) internally connected to copper wires of the pressed sheet for electrical access. In order to achieve uniform resistive heating, the composite is proposed to be used as individually addressable coupons that will be electrically heated by the healing circuit for healing. In addition, the electrical resistance of the carbon fiber bundles in the coupons is kept to a minimum to achieve faster heating and hence a quick healing response. The electrical resistance of the bundles measuring 20mm long is kept within 5–10 Ω . These self-healing coupons are targeted to be used as a healing layer.

The results demonstrate the ability of the polymer matrix to come together and close the path of penetration of a medium-velocity projectile (\approx 229 m/s). Subsequent heating of polymer using embedded carbon fibers demonstrates the ability of the polymer to further heal Smart Materials Research and close any damage from this impact. The polymer matrix made out of Surlyn melts at

95 °C from the heat generated in the carbon fiber layer and heals any surface and through thickness damage in the polymer matrix. The carbon fiber layer has low resistance and hence requires 2–3 W of electrical power in a 20 mm × 10 mm panel to heal any damage in the polymer. The mathematical model developed in this work characterizes the heating characteristics of Surlyn-carbon fiber composites for two configurations of carbon fiber in the polymer. Once the composite is heated and held near the glass transition temperature of the polymer matrix, the experiments show that a surface damage in the polymer can be healed completely. A new metric, referred to as width-heal ratio that characterizes the melt flow around the damage, has been developed to represent healing in the polymer. The experiments demonstrate the damage in the material can be completely healed (with a heal ratio (WHR) > 0.9) by heating the damaged area to the melt temperature in less than 30 s. Thus, a composite material made from Surlyn and carbon fibers that can be used as the self-healing layer for various aerospace applications.

Self-Healing coatings.

The global problem of metals and alloys corrosion is a complicated challenge that has bothered mankind for many years [94]. Polymer coating systems are classically applied on a metal surface to provide a dense barrier against the corrosive species. They are also applied for wood surface. Surface scratches are generated which develop micro-cracks, eventually leading to macroscopic damage that causes the coating to lose its aesthetic and protective functions. The use of a self-healing coating will increase the operational life of coatings and eliminate the need to frequently refinish damaged coatings. In addition to tremendous cost savings, this results in significant energy savings from fabrication and application of the coating materials and conserves supplies of raw wood, an important natural resource.

Smart coatings are regarded as the coatings of the future. The main purpose of smart coating is to integrate self-healing agents within the coating which lead to partial or full coating recovery from any impairment. Introduction of urea formaldehyde microcapsules incorporated with healing materials into the organic coating was firstly disclosed by N. Sottol [95] who succeeds in this field in the year 1993. Since that, many scientists worked in this hot topic leading to a lot of successful attempts of self-healing coatings. As a result three main mechanisms for accomplishing self-healing properties i.e. intrinsic, capsule and vascular strategies are commonly proposed.

Yang et al. have investigated good self-healing coating systems using microencapsulated epoxy resin, with excellent protective anti-corrosion coating and high effectiveness for steel substrate by incorporating microcapsules into paints [96]. The microcapsule shells with rough morphology strengthen the bonding between paint matrix and microcapsule. The drawback of this approach is that the preparation of capsules and loading them with

the catalyst and epoxy required about six steps which are complicated and time-consuming.

From the important strategies used to fabricate smart coatings with self-healing characteristics is employing of polyurea formaldehyde (PUF) microcontainers with polymerisable agents loaded in it in which the process of self-healing was stimulus by a crack-induced splitting of the embedded capsules [97]. Another drawback of the approach with microcontainers using is that the healing procedure can proceed only once.

A unique approach among the self-healing methods which can be used for self-healing coatings is a thermoset/thermoplastic mixture that offers crack sealing capacity when the material is heated, and the thermoplastic is able to diffuse across the crack boundary to repair the material and restore its mechanical and structural integrity after being damaged. Such technology based on a polyurethane wood coating system was successfully developed by Ou R. et al. [98]. Thermoplastic healing agent polycaprolactone (PCL) was used as self-healing phase allowing to repair the material and restore its mechanical and structural integrity after being damaged. Moreover, the nanoparticles can be added to the self-healing wood coating to enhance the mechanical properties, so there is no loss of hardness and related mechanical properties due to the presence of the thermoplastic. The nanoparticles can be, but are not limited to the following: an organo-modified clay, metal oxide, organo-modified metal oxide, graphene, and carbon nanotubes. Phase separation of the thermoplastic PCL and the thermoset polyurethane made of polyol and isocyanate occurs at the later stage of polymerization. The pre-neutralized hot prepolymer/thermoplastic (PCL) mixture was poured into water, resulting in an emulsion in the case of waterborn resin. The emulsion is then coated on the wood and cured by drying for one hour at room temperature and aging at 60 °C for 4 hours. Solvent born resin was thermally cured followed by UV curing. Such kind of self-healing polymer coatings are able to recover the original finish to between 85 and 95 % of the original gloss value, with only a brief application of heat.

Superhydrophobic surfaces were successfully fabricated on solid wood by spray coating of perfluoroalkyl methacrylic copolymer (PMC)/TiO₂ nanocomposites onto polydimethylsiloxane (PDMS) pre-coated wood substrates (Fig. 4) [99]. The coated surfaces exhibited exceptional repellency toward water as well as organic liquids with low surface tensions such as ethylene glycol (with contact angle 150°). The damaged surface from UV irradiation and sandpaper abrasion could restore its superhydrophobicity by a simple heat treatment. Besides, with the incorporated TiO₂ nanoparticles, the coated surface exhibited desirable photocatalytic efficiency in degrading organic contaminants and also showed enhanced photostability with obviously inhibited discoloration during UV exposure. Such mechanically durable, self-healing

the dynamic urea bonds [103]. Nevertheless, the investigated substances were soft materials with poor mechanical properties (a Young's modulus of ca. 1 MPa at room temperature). The follow-up study by the same authors described an improvement in the mechanical properties by using a denser polymer network, which could be completely depolymerized under thermal treatment, resulting in the formation of the educts [104]. Consequently, remendability as well as recyclability of the polymer network was possible. However, this behavior was associated with the nearly complete depolymerization of the network and, thus, a partial decrease in the mechanical integrity of the material.

Martin D Hager and co-authors investigated the reversibility of dynamic poly(methacrylate) systems crosslinked with dynamic urea moieties (PMA-U) and their corresponding self-healing properties (Fig. 5) [105]. A sterically hindered amine is utilized during polymerization due to its ability to open urea bonds during thermal treatment. The polymer network is obtained after a simple photopolymerization procedure. The tensile testing featured excellent mechanical properties (E-moduli between 0.34 and 0.97 GPa). However, according to the bulk-healing tests the healing efficiency based on the maximal stress values was 50%. IR- and Raman spectroscopies as well as DSC investigations of model compound showed that the urea bonds opened during thermal treatment at 100 °C, proving the reversibility of the urea bonds. Nevertheless, at much higher temperatures (150 °C), slight bond opening was also observed for synthesized PMA-U polymers. Complete opening of the bonds of these polymers would have resulted in an enormous loss in the mechanical performance.

One other example of a self-healing material with a high E-modulus (up to 4.55 GPa) was described by Wudl and co-workers, who utilized a highly crosslinked polymer network (E-modulus: 3 GPa) [106, 107]. The authors reported a healing efficiency of ~ 50% even under nearly complete depolymerization of the network owing to thermally reversible DA cross-links.

Self-healing adhesives.

Self-healing adhesives (SHAs) are materials with remarkable practical potential for long-term adhesion. However, reports are extremely limited because it is difficult to meet high strength and efficient self-healing properties.

Tang with co-authors in their study have introduced alternating rigid and flexible segments in the dynamic quaternization cross-links of poly(1,2,3-triazolium) vitrimer (VPTA) adhesives [108]. In consequence, the VPTA adhesive demonstrates particularly high adhesive strength of 23.7 MPa, compared to the reported SHAs (≤ 7.5 MPa). The adhesive joints of VPTA can self-heal after completely broken for 20 times, while maintaining strengths all above 10 MPa, which is rarely reported. Furthermore, this adhesive also exhibits excellent solvent resistance, high durability, and good creep resistance. The structural

design strategy may serve as a versatile method for polymers to prepare strong and efficient SHAs.

Urea-formaldehyde capsules were synthesized in micro and nano sizes, containing linseed oil, and were incorporated through epoxy coatings applied on C-steel panels. [109]. The smaller microcapsules created higher self-healing performance for the coating matrix. The concentration of the embedded microcapsules affected the self-healing capability samples containing 15 wt.% microcapsules showed higher corrosion resistance. Nano/micro capsules improved the self-healing performance, wet adhesion and corrosion resistivity rather than micro ones. Besides creation of self-healing ability, the capsule embedment also reduced the permeability of water through the film. Nevertheless, added microcapsules as well as increasing their concentration reduced the adhesion strength of the epoxy coating. Despite of this, the reducing of synthesized capsule size (by means of ultrasonic energy application and/or higher agitation rate) could compensate the adhesion weakening. That is why nano samples were the preferred choice.

Another attractive branch of self-healing adhesives is covalently reversible chemical cross-link based on chemical bonds that can be broken by external influences, mainly heat or radiation energy. The most studied covalently thermo-reversible systems are based on the Diels-Alder (DA) reaction, probably because it ensures fast kinetics and a high number of recycles with little, if any, degradation between 50 and 200 °C.

Among the many chemical groups able to react via DA mechanism the most investigated ones involve furan as diene and maleimide as dienophile. The reason for this resides probably in the fast kinetics, which renders them attractive for potential industrial application.

Self-healing coatings based on reversible polymer network systems can be used to actively heal a local damage by application of an external stimulus, breaking the reversible covalent bonds. The self-healing principle is based on the reversible Diels-Alder equilibrium reaction between furan and maleimide functional groups (Fig. 6) [110–112].

Increasing the temperature shifts the reaction equilibrium toward the breaking of the reversible bonds, destroying the network structure and allowing the sustained damage to be healed. Upon cooling, the reversible bonds are formed again and the polymer network structure is restored.

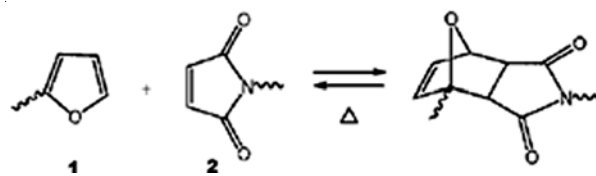


Fig. 6. Thermoreversible Diels-Alder equilibrium reaction between furan and maleimide

The Diels–Alder polymer networks reported by Wudl and co-workers depolymerized completely during thermal treatment, resulting in a very mobile phase and, consequently, in efficient self-healing behavior [107]. However, during depolymerization and formation of the educts, the mechanical integrity was partially lost.

Conclusions.

Self-healing materials are able to repair themselves when damaged, either autonomously or in response to external stimuli, and have potential to prolong the lifetime of materials. This article highlights the state of the art of self-healing materials for application as coatings and adhesives. Different methodologies of self-healing have been presented.

Extending the working life of the different structural and industrial metallic surfaces could be depending on the fabrication of novel self-healing protective smart-coatings which able to repair scratches and eliminate the corrosion. The importance of this category of coating that it can deal with respond to any internal or external stimulus and initiate the healing process. This makes the smart coatings very attractive materials for protection from corrosion especially in the places hard-to-reach. The self-

healing can heal scratches or damages on the metallic surfaces within a micro to millimeter scale range.

Some of the main issues related to self-healing materials for aerospace applications have been also analyzed. In particular, the attention has been focused on the development of self-healing materials to reduce the effect of the impact damage (mechanical stress, etc.) on the structural integrity of the material. For aeronautic applications, self-healing is not an alternative to the usual repair maintenance, but rather it is for repairing at the early stage of matrix microcracking and/or in the initial stage of delamination. Materials for aeronautic application are processed in very drastic conditions of temperatures. Furthermore, the operating temperature of the final materials ranges between -50 and $+60$ °C. Therefore the self-healing functionality must be assured at temperatures over this wide range.

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Самозаліковувані полімери: підходи заліковування та їх застосування

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В огляді стисло розглянуті дослідження, присвячені розробці та характеристиці полімерних самозаліковуваних матеріалів (Self-healing, S-H) з тривалим терміном служби, які здатні самостійно відновлюватись при пошкодженні без додаткового виявлення цього пошкодження та зовнішнього механічного втручання. Усі відомі підходи самозаліковування для полімерів можна розділити на дві групи: автономні та неавтономні. Автономне заліковування самостійне і не вимагає ніякого зовнішнього втручання, хоча в літературі цей метод також називають зовнішнім (extrinsic). Це пов'язано з наявністю в матеріалі додаткового заліковуючого агента, який розміщено в резервуарах. Залежно від концепції самовідновлення автономний підхід можна розділити на підгрупи, а саме: капсульних систем і систем мікровазкулярних або волоконних сіток. Неавтономне заліковування часткове; заліковуючу здатність закладено в матеріал, тому цей тип заліковування ще називають внутрішнім (intrinsic), але необхідні додаткові зовнішні фактори впливу, такі як тепло або ультрафіолетове випромінювання. Крім того, полімери внутрішнього самозаліковування можуть бути створені таким чином, щоб бути хімічно "липким" по лініях розриву, або відповідати різним енергетичним умовам, наприклад, бути чутливими до дії електромагнітного поля або проникнення кулі. Критично розглянуто переваги та недоліки кожного з підходів, запропонованих для створення S-H полімерних систем. Нові технології самовідновлення, розроблені з метою надання полімерним матеріалам здатності зупиняти розповсюдження тріщин на ранніх стадіях, запобігають катастрофічному пошкодженню цих матеріалів і допоможуть значно поширити сфери застосування цих матеріалів. Такі технології перспективні для створення супутників і космічних апаратів з функцією заліковування пошкоджень, які викликані високошвидкісними космічними уламками. Іншою перспективною галуззю застосування S-H полімерів, розглянутою в цьому огляді, є створення S-H покриттів та адгезивів. Крім того, висвітлюються проблеми та перспективи досліджень.

Ключові слова: «розумні» матеріали, самозаліковувані полімери, полімерні композити, адгезиви, покриття.

Самозалечивающиеся полимеры: подходы залечивания и их применение

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В этом обзоре кратко рассмотрены исследования, посвященные разработке и характеристике полимерных самозалечивающихся (Self-healing, S-H) материалов с длительным термином службы, которые способны самостоятельно восстанавливаться при повреждении без дополнительного выявления этого повреждения и внешнего механического вмешательства. Все известные подходы самозалечивания для полимеров можно разделить на две группы: автономные и неавтономные. Автономное самозалечивание является самостоятельным и не требует никакого внешнего вмешательства, хотя в литературе этот метод также называют внешним (extrinsic). Это связано с наличием в материале дополнительного залечивающего агента, помещенного в резервуары. В зависимости от концепции самозалечивания автономный подход можно разделить на подгруппы, а именно: капсульные системы и системы микроваскулярных или волоконных сетей. Неавтономное залечивание является частичным; залечивающая способность заложена в материал, поэтому этот тип залечивания еще называют внутренним (intrinsic), однако необходимы дополнительные внешние факторы воздействия, такие как тепло или ультрафиолетовое излучение. Кроме того, полимеры внутреннего самозалечивания могут быть созданы таким образом, чтобы быть химически “липкими” по линиям разрыва, или быть чувствительными к различным энергетическим условиям, например, воздействию электромагнитного поля или проникновению пули. Критически рассмотрены преимущества и недостатки каждого из подходов, предложенных для создания полимерных систем S-H. Новые технологии самовосстановления, разработанные с целью создания полимерных материалов со способностью останавливать распространение трещин на ранних стадиях, предотвращают катастрофическое повреждение таких материалов и помогут значительно расширить сферы использования этих материалов. Рассмотренные технологии S-H являются перспективными для создания спутников и космических аппаратов с функцией самовосстановления повреждений, вызванных высокоскоростными космическими обломками. Другой перспективной отраслью применения S-H полимеров, рассмотренной в этом обзоре, является создание S-H покрытий и адгезивов. Кроме того, освещены проблемы и возможности исследований в области создания S-H материалов.

Ключевые слова: «разумные» материалы, самозалечивающиеся полимеры, полимерные композиты, адгезивы, покрытия.