"HENRI COANDA"
AIR FORCE ACADEMY
ROMANIA

"GENERAL M.R. STEFANIK"
ARMED FORCES ACADEMY
SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER
AFASES 2012
Brasov, 24-26 May 2012

SELF-HEALING MATERIALS – FROM DESIGN TO SPECIFIC APPLICATIONS

Fulga TANASA, Madalina ZANOAGA

"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

Abstract: *Self-healing materials possess tremendous potential in increasing the longevity of structural materials. Consequently, a large number of academic and industrial research organizations have come forward to explore new concepts in design and synthesis of such materials. Though this field of innovative product research shows high promises, it has some practical limitations in understanding crack healing kinetics and stability of healing functionality. In this paper, different types of healing processes, design strategies and specific applications are reviewed.*

Keywords: *self-healing materials, autonomic process, non-autonomic process, design, applications*

1. INTRODUCTION

All materials, natural or synthetic, are susceptible to natural or artificial degradation. In the case of structural materials, the long-time degradation processes lead to microcracks that cause failure. Thus, repairing is indispensable to enhance reliability and lifetime of materials, especially when hi-tech industrial branches (aerospace and automotive industry, IT and robotics, healthcare, etc.) are involved. Though scientists are inspired by the natural process of blood clotting or repairing of fractured bones, incorporating the same concept into engineering materials is not fully possible due to the complexity of the healing processes in nature [1–4]. Self-healing phenomenon can be defined as the ability of a material to heal (recover/repair) damages, automatically and autonomously, without any external intervention. Many common terms such as self-repairing, autonomic-healing and autonomic-repairing are used to define such a property in materials. Incorporation of self-healing properties in man-made materials very often cannot perform the self-healing action without an external trigger. Based on these considerations, self-healing process can be of the following two types:

- autonomic (without any intervention);
- nonautonomic (needs human intervention or external triggering).

In the following section, the main design strategies for obtaining self-healing materials will be presented, as the most important tool is the concept of material microstructure and the relationship between microstructure and properties, processing, as well as applications.

2. DESIGN STRATEGIES

Materials science, one of the most fascinating and challenging branches of knowledge, is a multidisciplinary science. In understanding and designing materials with properties able to resolve specific tasks, physics, chemistry, engineering are employed.

The different types of materials (plastics, paints, coatings, metals and alloys, etc.) have their own self-healing mechanisms which depend on material microstructure.

The different strategies of designing self-healing materials are as follows: release of healing agent, reversible cross-links, miscellaneous technologies (electrohydrodynamics, conductivity, shape memory effect, nanoparticle migration, co-deposition).

2.1 Release of Healing Agents. Liquid active agents, such as monomers, dyes, catalysts and hardeners contained into microcapsules, hollow fibers or channels, are embedded into polymeric systems during manufacturing stage. In the case of a crack, these reservoirs are ruptured and the reactive agents are poured into the cracks by capillary force where it solidifies in the presence of predispersed catalysts and heals the crack. The propagation of cracks is the major driving force of this process. On the other hand, it requires the stress from the crack to be relieved, which is a major drawback of this process.

Microcapsule Embedment. Microencapsulation is a process of enclosing micron-sized particles of solids, droplets of liquids or gases in an inert shell, which, in turn, isolates and protects them from the external environments [5-7]. Healing agents or catalysts containing microcapsules are used to design self-healing polymer composites. Literature suggests the use of microencapsulated healing agents in a polyester matrix to achieve a self-healing effect. Recently, self-healing capabilities were achieved by embedding encapsulated healing agents into polymer matrix containing dispersed catalysts; i. e., dicyclopentadiene (DCPD) was used as liquid healing agent and Grubbs' catalyst [bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride] as internal chemical trigger, both of them dispersed in an epoxy matrix. The monomer is relatively less expensive and has high longevity and low viscosity [1, 8,9]. Figure 1 shows the self-healing mechanism of encapsulated DCPD and Grubb's catalyst.

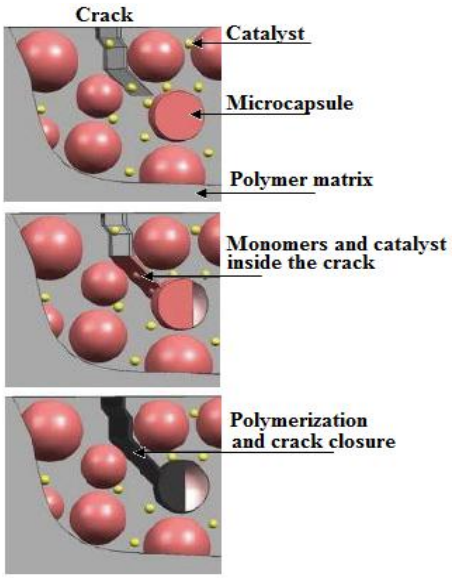

Fig. 1. Self-healing mechanism of the encapsulated DCPD and Grubb's catalyst

It was demonstrated that 75% of the fracture toughness recovery of compared to the original specimen can be achieved. Later, encapsulated catalyst was used instead of encapsulated monomer healing agent [10]. Monomers, such as hydroxyl-functionalized polydimethylsiloxane (HOPDMS) and polydiethyoxysilane (PDES), were added to vinyl ester matrix where they stay as microphase-separated droplets. The polyurethane microcapsules containing the catalyst di-*n*-dibutyltin dilaurate (DBTL) is then dispersed in the matrix. Polydimethylsiloxane (PDMS)-based self-healing elastomers using two different types of microcapsules have been designed [11], and the size of microcapsules on the self-healing efficiency was also investigated [12]. The critical factors that influence the microencapsulation-based self-healing approach to produce an effective self-healing material are summarized in Table 1.

Hollow Fiber Embedment. In order to achieve multiple healing, another type of reservoir that might be able to deliver larger amount of liquid healing agent was developed: capillaries; with only limited success, initially [13]. Later, large diameter capillaries were embedded into resins, but the trials were unsuccessful as well [14]. Smaller hollow glass fibers (Hollex fibers) filled with resin have been also used [15], but they were unable

to deliver the resin into the crack due to the high viscous epoxy resins.

Table. 1. Factors influencing the microencapsulation-based self-healing materials

Parameters	Factors of influence
Micro-capsules	Inertness towards the polymers shell Capsules lifetime Compatibility with the medium Weakness of the shell wall Proximity to the catalyst molecules Interfacial attraction strength between capsules and matrix
Monomers	Low viscosity Low volatility
Polymerization process	Rate of polymerization Stress relaxation Shrinkage Temperature
Catalysts	Solubility in monomer Dispersion
Coatings	Stability of properties upon incorporation of microcapsules Thickness Dispersion Processing
Healing effect	Rate of healing Repetitional

Later, a process to optimize the production of borosilicate hollow glass fibers (with diameters from 30 to 100 μm and hollowness of 55% - Fig. 2) was developed [16] and these fibers were used as containers for liquid healing agents and/or dyes [17].

The release and infiltration healing agent from fractured hollow fibers into the crack plane was also demonstrated.

This approach of offers certain advantages, as follows: higher volume of healing agent is available; different activation methods; visual inspection of the damaged site is feasible; hollow fibers can easily be mixed and tailored with the conventional reinforcing fibers.

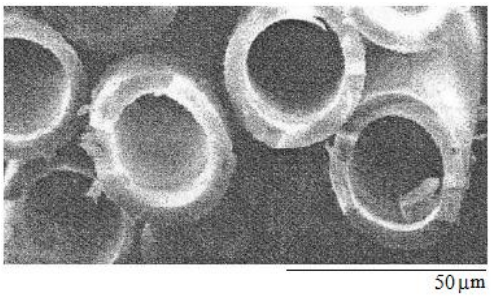

Fig. 2. Hollow fibers

Besides the above advantages, this approach has disadvantages as well: fibers must be broken to release the healing agent; low-viscosity resin must be used to facilitate fiber infiltration; use of hollow glass fibers in carbon fiber-reinforced composites will lead to problems concerning the coefficient of thermal expansion; multistep fabrication.

Microvascular System. This approach relies on a centralized network for distribution of healing agents into polymeric systems in a continuous pathway, in order to overcome the difficulty of short supply of the healing agent [18]. The fabrication process is complex and it is very difficult to achieve synthetic materials with such networks for practical applications.

2.2 Reversible cross-links. Polymeric materials having superior mechanical properties, but showing brittleness and tendency to crack, are usually obtained by cross-linking which is an irreversible process. One approach to bring processability to cross-linked polymers is the introduction of reversible cross-links in polymeric systems [19]. In addition, reversible cross-links also exhibit self-healing properties, but an external trigger, such as thermal, photo- or chemical activation) is needed. Thus, these systems show non-autonomic healing behaviour.

Diels–Alder (DA) and Retro-DA Reactions. Major classes of thermally reversible polymers are made using Diels–Alder (DA) reactions. Examples of this category include low temperature cross-linking of furanic polymers with maleimide or polymers containing maleimide pendants. Retro-DA reactions occur at elevated temperatures, evolve by debonding the chemical linkages of formed networks and yield in reversing the cross-linking process [20].

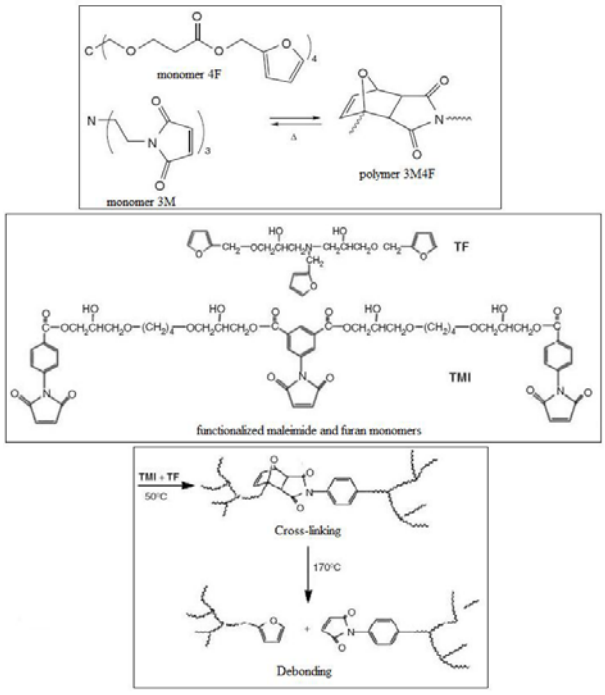

Fig. 3. Typical DA reactions

The [4+2] cycloadditions are the most studied thermally controlled covalent bond formation reactions. The first polymer where this strategy to design thermally remendable polymers was used is the polymer 3M4F, made of a multi-diene (4 furan moieties, 4F) and a multi-dienophile (3 maleimide moieties, 3M) [20], showing a strength recovery of 53-83%.

Modified polyamides having various amounts of maleimide and furan pendant groups have been used to obtain self-healing materials using DA and retro-DA reactions [21], but the prepared adduct does not show complete repairing of the cracks due to the low mobility of high molecular polyamide chains.

For the first time, the light-induced crack healing by the [2+2] photochemical cycloaddition of cinnamoyl groups has been reported [22]. The photochemical healing is very fast and does not require catalysts, additives or heat treatments.

Ionomers. Ionomers are a special class of polymeric materials that contain a hydrocarbon backbone and pendent acid groups, which are partially or fully neutralized to form salts. The polar ionic groups tend to aggregate as a result of electrostatic interactions, despite the opposing tendency of the chain elastic forces. The presence of ionic groups and their interactions produce physical reversible cross-links. As ionomers are not thermosetting materials, they can be processed like thermoplastics. The unique combination of physical properties and processability made this class of polymers fit to be used in food packaging, membrane separation, roofing materials, automobile parts, golf ball covers, coatings and, due to the reversible nature of ionic bonds, in designing of self-healing polymeric systems [23,24].

Supramolecular Polymers. Recently, low molar mass monomers are assembled together by reversible noncovalent interactions to obtain polymer-like rheological or mechanical properties [25-28]. Since noncovalent interactions can be reversibly broken and subjected to the thermodynamic equilibrium, these special materials, supramolecular polymers, show additional features (environment depending switch properties, improved processability, self-healing behaviour, etc.) compared to usual polymers. Some examples of supramolecular polymers (main- and side-chain types) are shown in Figure 4.

Different types of assembly forces, such as metal–ligand, hydrophobic, electrostatic and π–π interactions, as well as hydrogen bonding, are used to design supramolecular polymers. Hydrogen bonding is the most popular route of achieving supramolecular polymers. The main challenge in this approach is to find the right balance between the association constant and a reversible system. The higher the association constant, the lesser is the reversible interaction. In contrast, the lower the

association constant, the better the reversibility, but smaller assemblies and poor mechanical properties.

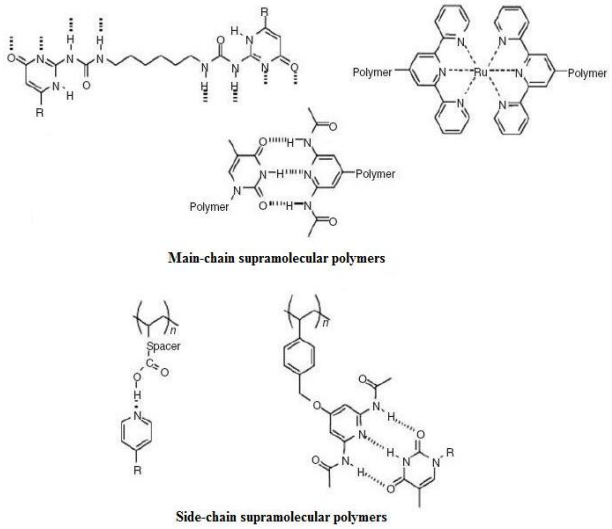

Fig. 4. Different types of supramolecular polymers

2.3 Miscellaneous Technologies. These emerging technologies, other than the most important design approaches already described, are presented herein.

Electrohydrodynamics. In this approach, the blood clotting process was mimicked *via* colloidal particle aggregation at the defected site, using the principle of electrohydrodynamics (EHD) flow, in order to design self-healing materials. The aggregation of particles is not sufficient to heal the defects as the voids between colloidal particles prevent formation of a dense surface.

A series of self-healing structural composites with electromagnetic functionality was also reported [29]. The self-healing effect is achieved through the contribution of all components, such as thermoreversible polymers, reinforcing fibers, and electromagnetic wires. In example, when fibers having negative CTE (coefficient of thermal expansion) is used to fill the core of the braid or fill in the weave of laminate, it will contract upon heating.

Conductivity. The tunable conductivities in polymeric materials can offer information on the structural integrity through electronic feedback that might give an insight to the most challenging task of detecting and quantifying microcracks. Thus, materials having conductivity, as well as self-healing capability, might be advantageous especially in deep sea or space applications. The conductivity, on the other hand, can also be used for inducing self-healing properties in polymeric systems.

Organometallic polymers based on *N*-heterocyclic carbenes and transition metals have been used to design electrically conductive self-healing materials [30]. These polymers exhibit structurally dynamic characteristics in the solid state and have good processability. When a microcrack is formed in a system, it decreases the number of electron percolation pathways and, thereby, an increase in electrical resistance.

Shape Memory Effect. Certain strongly ordered systems (alloys, ceramics, polymeric materials) show the shape memory effect, associated with self-healing properties, through different mechanisms [31].

Nanoparticle Migrations. It was demonstrated that nanoparticles suspended into a polymer fluid can segregate into cracks due to the polymer-induced depletion attraction between the particles and the surface [32]. The morphology obtained from the molecular dynamics simulations was used in a lattice spring model to determine the self-healing efficiency. The model predicts restoration of mechanical properties up to 75–100%. Self-healing materials based on this approach are yet to be demonstrated. Incorporation of nanoparticles into polymeric systems has advantages: it increases the

mechanical strength of the system and also segregates to the crack surface. Carbon nanotube is a potential candidate for developing self-healing materials based on this approach due to its superior mechanical properties compared to other particles.

Co-deposition. Electrolytic co-deposition can also be employed to design self-healing anticorrosive coatings. Microcapsules containing corrosion inhibitors can be added to composite plating coatings by this method [33].

3. APPLICATIONS AND CONCLUDING REMARKS

Currently, the self-healing materials development is enabled by the numerous research directions, so these materials will continue to find use in various applications, most of them in industry. Nowadays, the developed applications are mainly in the automotive, aerospace and building industries.

For example, Nissan Motor Co. Ltd has commercialized world's first self-healing clear coat for car surfaces, the "Scratch Guard Coat". This hydrophobic paint repairs scratches; depending on the depth of the scratch and the temperature in the surrounding environment, the entire recovery occurs between 1 and 7 days.

Another example in this category is the two component polyurethane clear coats from Bayer Material Science, Desmodur and Desmophen. This coating heals small scratches under the influence of heat (sunlight) and the principle employed to design such coatings is the use of dense polymer networks with flexible linkages.

The other industrial segment where applications of self-healing materials are foreseen is the aviation and space industry. Use of composites in aircrafts has grown significantly in the past years. Hollow fibers reinforced composites are a valid solution to recover cracking or damages. Self-healing polymers have also found uses in space applications.

Self-healing materials possess tremendous potential in increasing the longevity of structural materials. Consequently, a large number of academic and industrial research organizations have come forward to explore new concepts in this field. Though promising, the field of self-healing materials has some practical limitations in understanding crack healing kinetics and stability of healing functionality. Thus, the main challenge of self-healing material development is the autonomic detection of cracks and its subsequent healing.

The available technologies to design self-healing materials are not cost effective. This limits the wide use of these materials for different commercial applications. In future, new design strategies and technologies that will enable the possibility of using self-healing materials in our day-to-day life can be expected.

REFERENCES

1. Ghosh, S.K. (editor). *Self-healing Materials: Fundamentals, Design strategies and Applications.* Weinheim: Wiley-VCH (2009).
2. Fratzl, P., Weinkamer, R.. Hierarchical structure and repair of bone: deformation, remodeling, healing. In van der Zwaag S. (ed), *Self Healing Materials. An Alternative Approach to 20 Centuries of Materials Science*, Dordrecht: Springer (2007).
3. Vermolen, F.J., van Rossum, W.G., Javierre, E., Adam, J.A.. Modelling of Self Healing of Skin Tissue. In van der Zwaag S. (ed), *Self Healing Materials. An Alternative Approach to 20 Centuries of Materials Science*, Dordrecht: Springer (2007).
4. Kessler, M.R.. Self-healing: a new paradigm in materials design. *Proceedings of the Institution of Mechanical Engineers Part G-Journal of Aerospace Engineering*, 221 (2007).
5. Thies, C.. Microencapsulation. In Kroschwitz, J.I. (editor-in-chief) *Encyclopedia of Polymer Science and Engineering*, vol. 9, New York: John Wiley & Sons, Inc. (1987).
6. Benita, S.. *Microencapsulation: Methods and Industrial Applications*, New York: Marcel Dekker (1996).

7. Arshady, R.. *Microspheres, Microcapsules and Liposomes*, London: Citrus Books, (1999).
8. Shansky, E.. *Synthesis and Characterization of Microcapsules for Self-healing Materials*, Dept. of Chemistry, Indiana University, Bllomington (2006).
9. Tillner, S., Mock, U.. Korrosionsschutz - Mikrokapseln kitten Risse. *Farbe Und Lack*, 10 (2007).
10. Cho, S.H., Andersson, H.M., White, S.R., Sottos, N.R., Braun, P.V.. Poly-dimethylsiloxane-Based Self-Healing Materials. *Advanced Materials* 18 (2006).
11. Keller, M.W., White, S.R., Sottos, N.R.. An elastomeric self-healing material. In *Proceedings of the 2006 SEM Annual Conference and Exposition on Experimental and Applied Mechanics*, Society for Experimental Mechanics 1 (2006).
12. Rule, J.D., Sottos, N.R., White, S.R.. Effect of microcapsule size on the performance of self-healing polymers. *Polymer* 48 (2007).
13. Dry, C.M., McMillan, W.. Crack and damage assessment in concrete and polymer matrices using liquids released internally from hollow optical fibers. In *Procs of SPIE – Intl Society for Optical Engineering*. 2718 (1996).
14. Motuku, M., Vaidya, U.K., Janowski, G.M.. Parametric studies on self-repairing approaches for resin infused composites subjected to low velocity impact. *Smart Materials and Structures*. 8 (1999).
15. Bleay, S.M., Loader, C.B., Hawyes, V.J., Humberstone, L., Curtis, V.A.. Smart Repair System for Polymer Matrix Composites. *Composites A, Applied Science Manufacturing*. 32 (2001).
16. Hucker, M., Bond, I., Foreman, A., Hudd, J.. Optimisation of hollow glass fibres and their composites. *Advanced Composites Letters*. 8 (4) (1999).
17. Williams, H.R., Trask, R.S., Bond, I.P.. Vascular Self-Healing Composite Sandwich Structures. In The 15th US National Congress of Theoretical and Applied Mechanics. Boulder, Colorado, USA (2006).
18. Toohey, K.S., Sottos, N.R., Lewis, J.A., Moore, J.S., White, S.R.. Self-healing materials with microvascular networks. *Nature Materials*. 6 (2007).
19. Bergman, S.D., Wudl, F.. Remendable polymers. In van der Zwaag S. (ed), *Self Healing Materials. An Alternative Approach to 20 Centuries of Materials Science*, Dordrecht: Springer (2007).
20. Chen, X., Dam, A., Ono, K., Mal, A., Shen, H., Nutt, S.R., Sheran, K., Wudl, F.A.. Thermally Re-mendable Cross-Linked Polymeric Material. *Science*. 295 (2002).
21. Liu, Y.-L., Chen, Yi.-W.. Thermally Reversible Cross-Linked Polyamides with High Toughness and Self-Repairing Ability from Maleimide- and Furan-Functionalized Aromatic Polyamides. *Macromolecular Chemistry and Physics*. 208 (2007).
22. Chung, C.-M., Roh, Y.-S., Cho, S.-Y., Kim, J.-G.. Crack healing in polymeric materials via photochemical [2+2] cycloaddition. *Chemistry of Materials*. 16 (2004).
23. Kalista, S.J. Jr.. Self-healing of thermoplastic poly(ethylene-co-methacry-lic acid) copolymers following projectile puncture. Master Thesis. Virginia Polytechnic Institute and State University, Blacksburg, Virginia (2003).
24. Sun, C.X., van der Mee, M.A.J., Goossens, J.G.P., van Duin, M.. Thermoreversible cross-linking of maleated ethylene/

propylene copolymers using hydrogen bonding and ionic interactions. *Macromolecules*. 39(2006).
25. Bouteiller, L.. Assembly via hydrogen bonds of low molar mass compounds into supramolecular polymers. *Advances in Polymer Science.* 207 (2007).
26. Lehn, J.M.. Supramolecular polymer chemistry—scope and perspectives. *Polymer International*. 51 (2002).
27. Weck, M.. Side-chain functionalized supramolecular polymers. *Polymer International*. 56 (2007).
28. Shimizu, L.S.. Perspectives on main-chain hydrogen bonded supramolecular polymers. *Polymer International*. 56 (2007).
29. Plaisted, T.A., Amirkhizi, A.V., Arbelaez, D., Nemat-Nasser, S.C., Nemat-Nasser, S.. Self-healing structural composites with electromagnetic functionality. In Proceedings of Symposium on Industrial and Commercial Applications of Smart Structures Technologies, SPIE's 10th Annual International Conference on Smart Structures and Materials. Vol. 5054 (2003).
30. Williams, K.A., Boydston, A.J., Bielawski, C.W.. Towards electrically conductive self-healing materials. *Journal of the Royal Society of Interface*. 4 (2007).
31. Otsuka, K., Wayman, C.M. (editors). *Shape Memory Materials*, Cambridge: Cambridge University Press (1998).
32. Balazs, A.C., Emrick, T., Russell, T.P.. Nanoparticle polymer composites: where two small worlds meets. *Science*. 314 (2006).
33. Liqun, Z. Electrolytic co-deposition of polymer-encapsulated (microencapsulated) particles. In Ghosh, S.K. (editor) *Functional Coatings by Polymer Microencapsulation*. Weinheim: Wiley-VCH Verlag GmbH (2006).