International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.9, No.03 pp 316-324, 2016

Self Healing Composite Materials: A Review

J. Lilly Mercy*, S.Prakash,

Faculty of Mechanical Engineering, Sathyabama University, Chennai-600119, India

Abstract: Self-healing materials, sense the failure or damage and react autonomously to restore its structural integrity. Self healing mimicks biological systems where the body reacts to an external damage autonomously to heal the damage. Several researches have been done in the past decade identifying the healing capacity of several healing agents, its healing efficiency, the fracture toughness of the materials before and after healing. All classes of polymers, be it thermoplastics or thermosets or elastomers, have potential for self-healing. This paper focusses on bringing a short review to the readers on various types of healing processes, its uniqueness and its contribution towards the science of self healing.
Keywords: Self-healing materials, capsule based self healing, self healing chemistry, encapsulation, micro capsules, nanocapsules.

1. Introduction

Nature has succeeded in creating complex unexplainable systems, such as photosynthesis and the healing process within living organisms. Humans on the other hand are a relatively young species that have started rapidly advancing their scientific knowledge over the last two centuries. In the past we have looked at nature as a commodity and not a source of inspiration, but during the last ten years scientists have started to mimic nature by creating phenomenal materials that replicate the healing properties of organic systems. In the last 10 years there has been a huge influx of research on self-healing materials[1]. Researchers are attempting to find ways to mimic the healing process of living organisms and apply it to our infrastructure. This would create infrastructure that could potentially last forever.

There are three main types of materials that have been the focus of current research: polymers, concretes, and metals. Composites also offer advantages in terms of manufacturability, design flexibility, and part count reduction[2]. The major limitation of structural composites made from brittle polymers is their susceptibility to matrix micro-cracking when subjected to impacts, excessive forces, and cyclic mechanical and/or thermal loads[3]. Micro-cracks also instigate other forms of damage through coalescence, including fiber/matrix de-bond, ply delamination, and fiber break, or provide pathways for entry of corrosive liquids[4-7]. Biology provides an abundance of self-healing systems that specify the basic principles behind the design of healing systems. The initial response of damage is triggered by injury. Biological response is threefold: inflammatory response (immediate), cell proliferation (secondary), and matrix remodeling (long-term). Synthetic systems share this three-step process, albeit in a more simplistic fashion and at an accelerated rate. The first response is triggering (actuation), which is closely coupled to the timescale of damage. The second response is transport of materials to the site of damage, again at a relatively rapid rate. The third response, analogous to matrix remodeling, is the chemical repair process, at a timescale that is dependent on the type of healing mechanism employed (e.g., polymerization, entanglement, reversible cross-linking)[8]. The first overview of self-healing materials in 2007 contained multiple chapters written by leading researchers in the field of self healing and covered a wide range of materials from polymers to metals and ceramics[9].

Since that time, many articles focussing on self-healing materials have appeared in the literature[10-19]. Bergman & Wudl[10] described in detail intrinsic healing in polymers and their mechanisms. Wool's contribution[11] attempted to provide a general theory of damage and healing for polymers, drawing from the related field of polymer-polymer interfaces. Wu et al[12] offered a primer on the fracture mechanics and mechanisms of healing in polymeric systems. The reviews by Kessler[13] and Yuan et al[14] are more general and provide context for ongoing research in the field. In addition, a recent *MRS Bulletin* was devoted to self- healing polymers[15], with contributions summarizing self-healing chemistries[16], polymers[17], and composite systems[18]. Trask et al[19]also provided a recent perspective on self-healing fiber-reinforced composites (FRCs).

This reversible self-healing crack element was used to examine some of basic phenomena of an idealized self-healing element, which could be used in series or parallel with elementary springs and dashpots, similar to the Maxwell or Voigt models. It consisted of two surfaces with an anharmonic potential function V(l) which would permit yielding at a critical strain$\epsilon_c = \lambda c\text{-}1$[20]. Such self-healing material with most peculiar mechanical properties, such as negative creep compliances J(t) and reactive stress relaxation moduli G(t) where the stress would first decrease with time and then suddenly increase at constant strain can now be made with intercalated nanoclays and carbon nanotube bundles[21-23].

2. Approaches to Self-healing

Self-healing materials can be broadly classified into three categories, namely: capsule based, vascular and intrinsic[24]. This section presents an overview of the approaches that have been employed to prepare self-healing materials and the salient features for each approach.

Capsule-based self-healing materials *(Figure 1*) supply the healing agent in a finite number of capsules. When the capsules are ruptured by a crack or damage, the self-healing mechanism is triggered which releases the healing agent in the region of damage. After release, the local healing agent reacts with the catalyst to yield a toughened polymerised network.

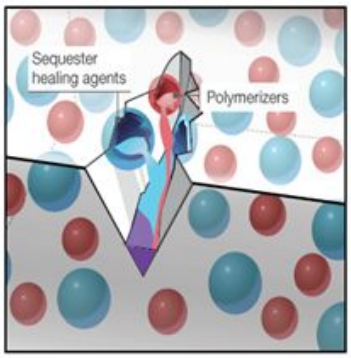

Figure 1: Capsule based self-healing agent[8]

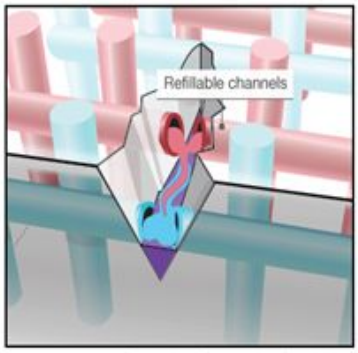

Figure 2: Vascular self-healing agent[8]

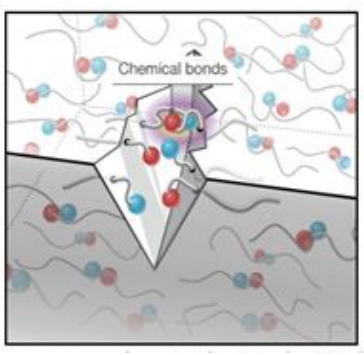

Figure 3: Intrinsic self-healing agent[8]

Vascular self-healing materials *(Figure 2)* sequester the healing agent in a network in the form of capillaries or hollow channels, which may be interconnected one-dimensionally (1D), two-dimensionally (2D), or three-dimensionally (3D), until damage triggers self-healing. After the vasculature is damaged and the first delivery of healing agent occurs, the network may be refilled by an external source or from an undamaged but connected region of the vasculature. This refilling action allows for multiple local healing events.

Intrinsic self-healing materials (*Figure 3*) do not have a seperate healing agent but possess a self-healing mechanism that is triggered by damage or by an external stimulus. These materials rely on chain mobility and entanglement, reversible polymerizations, melting of thermoplastic phases, hydrogen bonding, or ionic interactions to start with the self-healing process. Because each of these reactions is reversible, multiple healing events are possible.

2.1 Self-Healing Chemistry for the Nanoscale

Three potential healing chemistries have been identified (1) Grubbs catalyzed DCPD monomer, (2) one-part solvent epoxy, and (3) two-part amine cured epoxy[25]

2.1.1Grubbs catalyzed DCPD monomer

Capsules containing DCPD monomers are prepared by *in situ* polymerization of urea and formaldehyde using a modified process of Brown *et al*[26]. Images of the nanocapsules show spherical capsules, free of surface debris with well-formed shell walls (*Figure 4*).

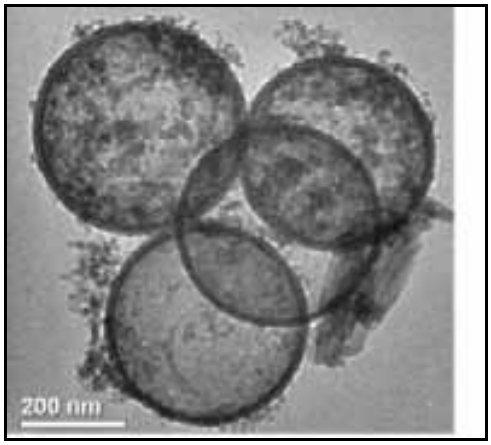

Figure 4: TEM image showing the core-shell morphology of the nanocapsules[25]

2.1.2 One-part solvent epoxy

Nanocapsules containing a solvent and reactive epoxy resin hold promise for the development of cost-effective, low toxicity, and low flammability self-healing materials[27,28]. Capsules as small as 300 nm in diameter can be achieved through sonication and stabilization procedures[29]. These capsules were used to functionalize high performance fibers for interfacial healing studies.

2.1.3 Two-part amine cured epoxy

Microencapsulation of a reactive amine represents a leap forward in self-healing chemistry in an epoxy matrix. As most advanced composite materials rely on the ring-opening reaction of epoxide with amine, a two-part healing chemistry that incorporates identical material to the existing matrix is mostly accepted[30]. Present research demonstrated that an amine phase can be emulsified and a thin shell can be formed around the amine droplet. Work is still in progress to establish the healing efficiency of these systems.

3. Capsule based Self-healing materials

Capsule-based self-healing materials (*Figure 1*) sequester the healing agent in discrete capsules until damage triggers rupture and release of the capsule contents. In this section, a range of encapsulation techniques, the capsule-based material design cycle, and example capsule-based systems are described.

3.1 Encapsulation methods

A variety of techniques exist for encapsulation of reactive materials. These techniques can be classified as interfacial, in situ, coacervation, meltable dispersion or physical on the basis of the mechanism of wall formation. A thorough description of these techniques is outside the scope of this review, but reviews of encapsulation techniques can be found in literature for food science, medical, industrial, and agricultural applications[31-33].

For self-healing materials, the most common encapsulation techniques are in situ, interfacial, and meltable dispersion. In situ and interfacial encapsulations proceed by reaction of urea-formaldehyde (UF)[34-38], melamine-formaldehyde (MF)[39–41], melamine-urea-formaldehyde (MUF)[42], polyurethane (PU)[43], or acrylates[44] and the subsequent formation of polymer shell wall at the interface of droplets in an oil-in-water (o/w) emulsion. Meltable dispersion encapsulations proceed by dispersion of the active core in a melted polymer. The melted polymer is emulsified to form droplets and solidified by temperature change or solvent removal to form a protective sphere around the core[45]. Core-shell capsules have also been prepared by inverse emulsion[46],

Pickering stabilization[47], inverse Pickering stabilization[48], and multiple emulsions[49] in the literature but have not been used to date for self-healing materials.

3.1.2 Design Cycle of Capsule based Material

The design cycle are classified into five steps: development, integration, mechanical characterization, triggering, and healing evaluation[8]. The summarised review of Blaiszik et al[8] is discussed below to explore the design cycle of capsule based systems.

The first challenge is determining the optimal method for conveying the healing agent and catalyst. This can be done through encapsulation of either the healing agent or the catalyst.

The main considerations for the effective healing agent are the solubility, reactivity, viscosity, volatility, and pH of the material. Although these properties describe the ideal healing agent, alternate encapsulation methods may allow for healing agents or polymerizers that do not meet these criteria. This forms the first phase of development.

The next consideration is integration. The shear forces induced on the surface of the capsules during mixing, processing temperature, capsule-matrix reactivity, and size scale of the capsulesvary and has effect on the smooth formation of the microcapsules. UF, MF/MUF, and PU capsules used commonly for self-healing polymeric composites, have shown an ability to survive processing conditions in common thermoset resin matrices and composite manufacturing processes which makes these materials as common healing agents.

After the capsules are incorporated into the material, the mechanical properties, triggering mechanism, and healing performance can be characterized. The interfacial bonding of capsules with the matrix, the capsule-matrix volume fraction, and the capsule toughness may affect mechanical properties of the self-healing material such as fracture strength, fracture toughness, and elastic moduli.

The triggering mechanism can be proved by observation of capsule rupture and release in situ observation of the release of healing agent on the crack plane, and the ruptured capsules, by infrared spectroscopy (IR)[50], by scanning electron microscopy (SEM)[50] and energy-dispersive X-ray spectroscopy (EDS)[50] of the fracture plane. Self-healing performance can be evaluated by various testing methods, depending on theapplication it has been put into. For example, polymers and composites used in structural applications are commonly measured for their fracture toughness, stiffness, or other mechanical properties.

The healing performance of self-healing system is dependent on the volume of damage, damage and healing rate, healing temperature, and bond strength between the healed material and the matrix material. Direct evidence of healing may also be observed by optical microscopy, IR, or SEM techniques (*Figure 5*).

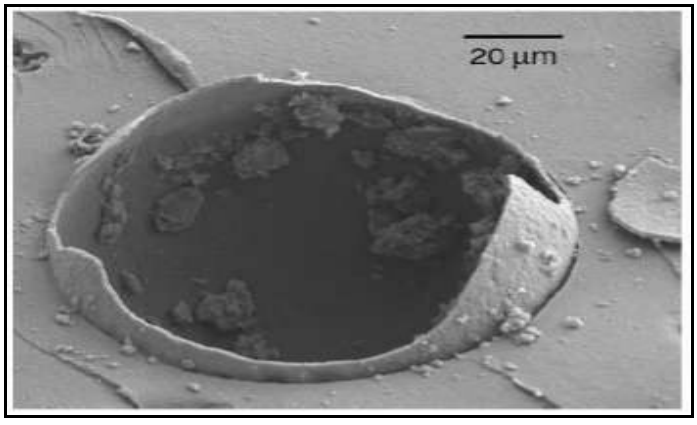

Figure 5: SEM micrograph of a fracture surface showing a broken microcapsule embedded in a thermosetting polymer matrix. Microcapsule diameter is approximately 100µm[19].

Self-healing polymers and composites that use microencapsulated healing agents have shown high levels of healing efficiency in both static and dynamic loading conditions[51-53,34]. Capsule-based self-healing

materials have been developed for some of the most commonly used synthetic polymers and elastomers using a variety of capsule-based sequestration schemes. Each scheme sequesters a healing agent in a discrete capsule until damage triggers release **(***Figure 6***)**.

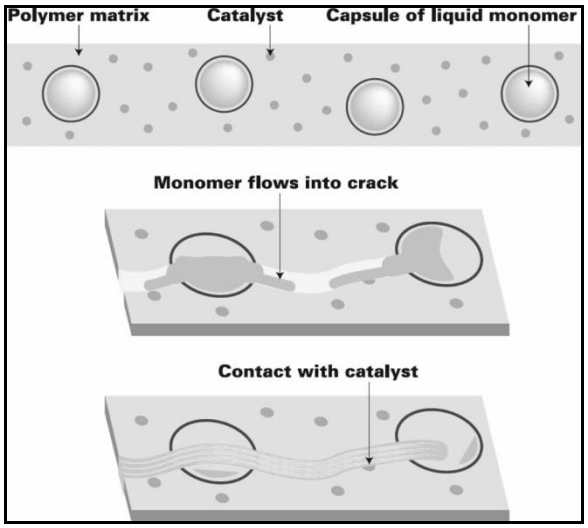

Figure 6: The self-healing concept using embedded microcapsules. A microencapsulated liquid monomer healing agent is embedded in a structural polymer matrix containing a catalyst capable of polymerizing the healing agent. When the material is damaged cracks occur, rupturing the microcapsules and releasing the healing agent into the crack plane through capillary action. The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed[13].

The figure shows that the healing agent is an encapsulated liquid and the polymerizer is a dispersed catalyst phase. An example capsule-catalyst system is the dicyclopentadiene (DCPD)-Grubb's catalyst system of White et al[53].

This system heals on the basis of the ring-opening metathesis polymerization (ROMP) of DCPD when it comes in contact with the Grubbs' catalyst. In the previous literature using this healing system, Brown et al[54] reported high healing efficiencies, fatigue life extension[55,56] and a significant quasi-static toughening effect[57]. This DCPD-Grubbs' self-healing system has been incorporated into bulk matrices of epoxy[26,53-61], fiber reinforced epoxy composite[62-65] and thermoplastic-elastomeric copolymers[66]. Computational study of this self healing mechanism has also been studied[67]. Wilson et al[68] examined various catalysts, and Liu et al[69] tested a variety of diene monomers for self-healing potential. Moll et al[62] developed a self-healing composite by incorporating DCPD-filled capsules and wax protected Grubbs' catalyst spheres into a glass fiber-reinforced epoxy composite.

4. Mechanical Properties of Capsule/Epoxy composite

4.1 Elastic Modulus and Tensile Strength

Measurements of the elastic modulus were obtained by dynamic mechanical analysis (DMA). The elastic modulus of the capsule filled composite was measured and compared between various capsule sizes and capsule volume fractions.

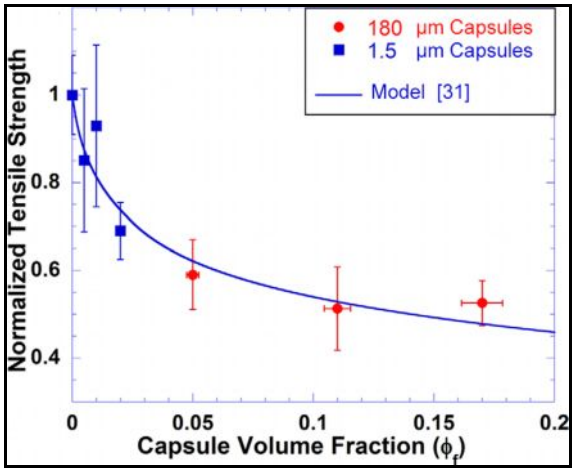

Figure 7: Tensile strength of epoxy/capsule composite for large diameter capsules[70].

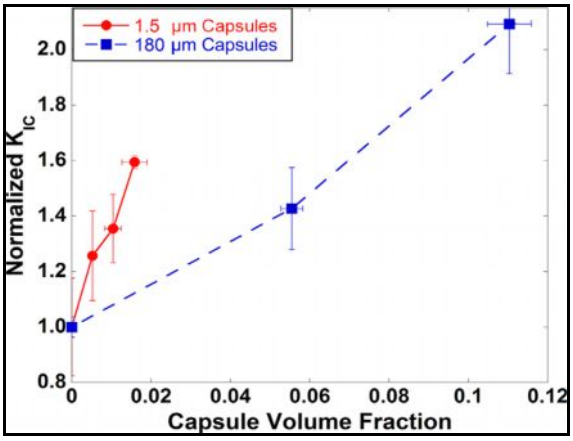

Figure 8: Fracture toughness of epoxy/capsule composite with 1.5 µm capsules compared to data gathered previously by Brown et al. using 180 µm capsules [71].

Very little change in modulus from the neat resin was observed with the addition of 0.5–2.0% volume fraction of the 1.5 µm capsules[72]. As shown in *Figure 7*, a drop in tensile strength was observed for capsule loadings up to $Ø_f$ = 0.02. For comparison, the data from previous investigations of 180 µm capsules is also plotted in *Figure 8*[73].

The interrelation of tensile strength and average filler particle diameter was studied by Landon et al[74] for a cross-linked polyurethane composite. Their studies suggest that smaller particles have less of an effect on the tensile strength. Change in tensile strength was not observed with the change in capsule diameter within their measured range.

4.2 Fracture toughness

The mode-I fracture toughness (K_{IC}) of the epoxy with capsule composite was investigated over a range of capsule concentrations. As shown in Figure 8, K_{IC} increased significantly with capsule volume fraction ($Ø_f$). A 59% increase in fracture toughness was achieved for $Ø_f$ = 0.015. The current data for sonicated capsules (ca. 1.5 µm diameter) were also compared to data taken by Brown et al. for larger capsules (ca. 180 µm diameter)[75]. As shown in Figure 8, the increase in fracture toughness per volume fraction of capsules was substantially higher for 1.5 µm capsules than for larger capsules.

5. Conclusions

Over the past decade, research on self-healing polymers and composites and for multiple material systems were done encompassing a wide variety of damage modes, self-healing concepts, different base matrices and with a wide variety of healing agents. And the progress in this field still continues to yield new healing chemistries that possess greater stability, higher reactivity, and faster kinetics. Self-healing composites possess great potential for solving some of the most limiting problems of polymeric structural materials: microcracking and hidden damage. Microcracks are the precursors to structural failure[76] and the ability to heal them will enable structures with longer lifetimes and less maintenance. Several other approaches to achieving self-healing are also being explored. For example, several groups have investigated the use of shapememory alloy actuators to close and heal cracks[77-79]. While many different approaches to imparting selfhealing functionality to polymers and composites are being explored, and others will undoubtedly emerge, nearly all of them are intrinsically multidisciplinary. They involve the challenge of combining polymer science, experimental and analytical mechanics, and composites processing principles. Perhaps the best systems will be hybrid techniques which span the multiple lengths and time scales of the different approaches. Certainly the nascent field of self-healing synthetic materials will continue to progress beyond the methods reviewed here, until true biomimetic healing is achieved.

References

1. M.D Hager, P. Greil & C Leyens, Advanced materials Self-healing materials, Weinheim: Wiley-VCH (2010) pp. 5424–5430.
2. M.R. Kessler,Self-healing: a new paradigm in materials design, Proc.Inst. Mech. Eng. G: J. Aerospace Engineering, Vol. 221(2007) pp 479-495**.**
3. J.ANairn, Matrix microcracking in composites, In Polymer matrix composites (Eds Talreja R. and Månson J.A.E.), in Comprehensive composite materials, vol. 2 (2000)pp. 403–432.
4. R. Talreja, Damage development in composites: mechanisms and modelling, J. Strain Analysis, 24 (1989)215–222.
5. R. Talreja, (Ed.), Damage mechanics of composite materials, (Elsevier Press, New York), 1994
6. E.K Gamstedt, and R. Talrega, Fatigue damage mechanisms in unidirectional carbon-fibre-reinforced plastics. Journal of Material Science, 34(1999) 2535–2546.
7. L. Hollaway, Polymer composites for civil and structural engineering, (Blackie Academic and Professional,an imprint of Chapman and Hall, London), 1993
8. B.J Blaiszik, S.L.B Kramer, S.C Olugebefola, J.S Moore, N.R Sottos and S.R White, Self-Healing Polymers and Composites, Annual Review of Materials Research, volume 40 (2010) pp. 179-211.
9. S. van der Zwaag, Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science.Dordrecht: Springer-Verlag, 2007.
10. S.D Bergman, F. Wudl, Mendable polymers, Journal Material Chemistry 18(1) (2008) 41–62.
11. R.P Wool, Self-healing materials: a review, Soft Matter 4(3) (2008) 400–18.
12. DY Wu, S Meure, D. Solomon, Self-healing polymeric materials: a review of recent developments, Program of Polymer Science, 33(5) (2008) 479–522.
13. M.R Kessler, Self-healing: a new paradigm in materials design. Proc. Inst. Mech. Eng. G 221(4) (2007) 479–495.
14. Y.C Yuan, T. Yin, M.Z Rong, M.Q Zhang, Self-healing in polymers and polymer composites. Concepts, realization and outlook: a review. Express Polym. Lett. 2(4) (2008) 238–50
15. J.P Youngblood, N.R Sottos, C. Extrand, Bioinspired materials for self-cleaning and self-healing, MRS Bull. 33(8) (2008) 732–41
16. K.A Williams, D.R Dreyer, C.W Bielawski, The underlying chemistry of self-healing materials, MRS Bull. 33(8) (2008) 759–65.
17. S.R White, M.M Caruso, J.S Moore, Autonomic healing of polymers. MRS Bull. 33(8) (2008) 766–69
18. I.P Bond, R.S Trask, H.R Williams, Self-healing fiber-reinforced polymer composites. MRS Bull, 33 (2008) 770–74.
19. R.S Trask, H.R Williams, I. P Bond, Self-healing polymer composites: mimicking nature to enhance performance. Bioinspiration Biomim. 2(1) (2007) 1–9.
20. R.P Wool, Self-healing materials: a review, Soft Matter, 4 (2008) 400–418.
21. R.P Wool and X.S Sun, Bio-based Polymers and Composites, Elsevier, Burlington, MA, 2005
22. L. Zhu and R.P Wool, ‘‘Biodegradable Elastomers from Plant Oils’’, Abstract Paper for American Chemistry Society, 230 (2005) U3766–U3767, 553-PMSE.
23. L. Zhu and R.P Wool, Polymer, 47(24) (2006) 8106–8115.
24. B.J Blaiszik, S.L.B Kramer, S.C Olugebefola, J.S Moore, N.R Sottos and S.R White, Self-Healing Polymers and Composites, Annual Review of Materials Research, volume 40 (2010) pp. 179-211.
25. Nancy R. Sottosand Paul V. Braun, Nanostructured Self-Healing Polymers and Composites, AF Grant # FA9550-06-1-0553, 2010.
26. E.N Brown, M.R Kessler., N.R Sottos. and S.R. White, In situ poly(urea formaldehyde) microencapsulation of dicyclopentadiene. J. Microencapsulation, 20 (2003) 719-730.
27. M.M Caruso., D.A Delafuente., V. Ho, J.S Moore, N.R Sottos, and S.R White, Solvent- Promoted Self-Healing Materials, Macromolecules 40 (2007) 8830-8832.
28. M.M Caruso, B.J Blaiszik, S.R White, N.R Sottos, J.S. Moore, Full recovery of fracture toughness using a non-toxic solvent-based self-healing system, Advanced Functional Materials, Cover Feature, 18 (2008) 1898-1904.
29. B. Blaiszik, M Caruso, D McIlroy, J. Moore, S. Whiteand N.R Sottos, Microcapsules filled with reactive solutions for self-healing materials, Polymer, 50, (2009), 990-997.

30. D.A McIlroy, B.J Blaiszik, M.M Caruso, S.R White, J.S Moore, N.R Sottos, Microencapsulation of a Reactive Liquid-Phase Amine for Self-Healing Epoxy Composites, Macromolecules, 43 4(2010) 1855–1859.
31. A. Kond¯o, J.W Van Valkenburg, Microcapsule Processing and Technology, New York: Marcel Dekker, 1979
32. S. Benita, ed., Microencapsulation: Methods and Industrial Applications. Boca Raton, FL: CRC/Taylor & Francis, 2006
33. S.K Ghosh, ed., Functional Coatings: By Polymer Microencapsulation, Weinheim: Wiley-VCH, 2006
34. B.J Blaiszik, N.R Sottos, S.R White, Nanocapsules for self-healing materials. Composite Science Technology 68(3–4) (2008) 978–86.
35. B.J Blaiszik, M.M Caruso, D.A McIlroy, J.S Moore, S.R White, N.R Sottos, Microcapsules filled with reactive solutions for self-healing materials. Polymer 50(4) (2009) 990–97.
36. M.W Keller, S.R White, N.R Sottos, A self-healing poly(dimethyl siloxane) elastomer. Adv. Funct. Mater. 17(14) (2007) 2399–404.
37. L. Yuan, G.Z Liang, J.Q Xie, L. Li, J. Guo, Preparation and characterization of poly(urea-formaldehyde) microcapsules filled with epoxy resins. Polymer 47(15) (2006) 5338–49.
38. S. Cosco, V. Ambrogi, P. Musto, C. Carfagna, Properties of poly(urea-formaldheyde) microcapsules containing an epoxy resin. J. Appl. Polym. Sci. 105(3) (2007) 1400–11.
39. Y.C Yuan, M.Z Rong, M.Q Zhang, B. Chen, G.C Yang, X.M Li, Self-healing polymeric materials using epoxy/mercaptan as the healant. Macromolecules 41(14) (2008) 5197–202.
40. Y.C Yuan, M.Z Rong, M.Q Zhang, Preparation and characterization of microencapsulated polythiol, Polymer 49(10) (2008) 2531–41.
41. Y.C Yuan, M.Z Rong, M.Q Zhang, Preparation and characterization of poly (melamine-formaldehyde) walled microcapsules containing epoxy. Acta Polym. Sin. (5) (2008) 472–80.
42. X. Liu, X. Sheng, J.K Lee, M.R Kessler, Synthesis and characterization of melamine-urea-formaldehyde microcapsules containing ENB-based self-healing agents, Macromol. Mater. Eng. 294(6–7) (2009) 389–95.
43. S.H Cho, H.M Andersson, S.R White, N.R Sottos, P.V Braun, Polydimethylsiloxane-based self-healing materials. Adv. Mater. 18(8) (2006) 997–1000.
44. DS Xiao, Y.C Yuan, M.Z Rong, M.Q Zhang, Hollow polymeric microcapsules: preparation, characterization and application in holding boron trifluoride diethyl etherate. Polymer 50(2) (2009) 560–68.
45. J.D Rule, E.N Brown, N.R Sottos, S.R White, J.S Moore, Wax-protected catalyst microspheres for efficient self-healing materials. Adv. Mater. 17(2) (2005) 205–8.
46. C.K Yeom, S.B Oh, J.W Rhim, J.M Lee, Microencapsulation of water-soluble herbicide by interfacial reaction. I. Characterization of microencapsulation. J. Appl. Polym. Sci. 78(9) (2000), 1645–55
47. S.D Mookhoek, B.J Blaiszik, HR Fischer, NR Sottos, SR White, S. van der Zwaag Peripherally decorated binary microcapsules containing two liquids. J. Mater. Chem. 18(44), (2008), 5390–94.
48. DJ Voorn, W Ming, AM. Van Herk, Polymer-clay nanocomposite latex particles by inverse pickering emulsion polymerization stabilized with hydrophobic montmorillonite platelets. Macromolecules, 39(6) (2006) 2137–43.
49. AR Abate, DA. Weitz, High-order multiple emulsions formed in poly (dimethylsiloxane) microfluidics. Small 5(18) (2009) 2030–32.
50. SR White, NR Sottos, PH Geubelle, JS Moore, MR Kessler, Autonomic healing of polymer composites. Nature 409(6822) (2001) 794–97.
51. EN Brown, NR Sottos, SR. White, Fracture testing of a self-healing polymer composite. Exp Mech; 42(4) (2002) 372–9.
52. EN Brown, SR White, NR. Sottos, Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite – Part II: In situ self-healing. Comp Sci Tech ; 65(15-16) (2005) 2474–80.
53. MR Kessler, NR Sottos, SR. White Self-healing structural composite materials. Compos Part A Appl Sci Manuf; 34(8) (2003) 743–53.
54. EN Brown, NR Sottos, SR. White, Fracture testing of a self-healing polymer composite. Exp. Mech. 42(4) (2002) 372–79.
55. EN Brown, SR White, NR Sottos, Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite. 1. Manual infiltration. Compos. Sci. Technol. 65(15–16) (2005) 2466–73.

56. EN Brown, SR White, NR. Sottos, Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite. II. In situ self-healing. Compos. Sci. Technol. 65(15–16) (2005) 2474–80.
57. EN Brown, SR White, NR Sottos, Microcapsule induced toughening in a self-healing polymer composite. J. Mater. Sci. 39(5) (2004) 1703–10.
58. JD Rule, NR Sottos, SR White, Effect of microcapsule size on the performance of self-healing polymers. Polymer 48(12) (2007) 3520–29.
59. EL Kirkby, JD Rule, VL Michaud, NR Sottos, SR White, JAE Manson, Embedded shape-memory alloy wires for improved performance of self-healing polymers. Adv. Funct. Mater. 18(15) (2008) 2253–60.
60. AS Jones, JD Rule, JS Moore, NR Sottos, SR White, Life extension of self-healing polymers with rapidly growing fatigue cracks. J. R. Soc. Interface 4(13) (2007) 395–403.
61. EL Kirkby, VJ Michaud, JAE Manson, NR Sottos, SR. White, Performance of self-healing epoxy with microencapsulated healing agent and shape memory alloy wires, Polymer 50(23) (2009) 5533–38
62. JL Moll, SR White, NR. Sottos, A self-sealing fiber reinforced composite. J. Compos. Mater. Inpress; doi: 10.1177/0021998309356605, 2010.
63. MR Kessler, NR Sottos, SR. White, Self-healing structural composite materials. Composites A 34(8) (2003) 743–53.
64. AJ Patel, NR Sottos, ED Wetzel, SR. White, Autonomic healing of low-velocity impact damage in fiber-reinforced composites. Composites A 41(3) (2010) 360–68.
65. MR Kessler, SR. White, Self-activated healing of delamination damage in woven composites. Composites A 32(5) (2001) 683–99.
66. MD Chipara, M Chipara, E Shansky, JM. Zaleski, Self-healing of high elasticity block copolymers. Polym. Adv. Technol. 20(4) (2009) 427–31.
67. S Maiti, PH. Geubelle, Cohesive modeling of fatigue crack retardation in polymers: crack closure effect. Eng. Fract. Mech. 73(1) (2006) 22–41.
68. GO Wilson, MM Caruso, NT Reimer, SR White, NR Sottos, J. S Moore, Evaluation of ruthenium catalysts for ring-opening metathesis polymerization-based self-healing applications. Chem.Mater. 20(10) (2008) 3288–97.
69. X Liu, JK Lee, SH Yoon, MR. Kessler, Characterization of diene monomers as healing agents for autonomic damage repair. J. Appl. Polym. Sci. 101(3) (2006) 1266–72.
70. RD. Sudduth, Analysis of the maximum tensile strength of a composite with spherical particulates. J Compos Mater; 40(4) (2006) 301–31.
71. EN. Brown, Fracture and fatigue of a self-healing polymer composite material. PhD Thesis, University of Illinois at Urbana-Champaign, Department of Theoretical and Applied Mechanics, 2003.
72. B.J Blaiszik., N.R Sottos., S.R. White, Nanocapsules for self-healing materials, Composites Science and Technology 68 (2008) 978–986.
73. AA Rzesutko, EN Brown, NR Sottos, Tensile properties of selfhealing epoxy. TAM Tech Rep: (2003) 1041–55.
74. G Landon, G Lewis, GF. Boden, The influence of particle size on the tensile strength of particulate-filled polymers. J Mater Science; 12(8) (1977) 1605–13
75. EN Brown, NR Sottos, SR. White, Fracture testing of a self-healing polymer composite. Exp Mech; 42(4) (2002) 372–9.
76. J. A Nairn, Matrix microcracking in composites. In Polymer matrix composites (Eds R. Talreja and J.-A. E. Manson), in Comprehensive composite materials, vol. 2 **(**2000) pp. 403–432.
77. D. S Burton, X. Gao, and L. C. Brinson, Finite element simulation of a self-healing shapememory alloy composite. Mech. Mater., 38 (2006) 525–537.
78. S. Araki, H. Ono, and K. Saito, Micromechanical analysis of crack closure mechanism for intelligent material containing TiNi fibers. JSME Int. J. A, Solid Mech. Mater.Eng., 45 (2002) 208–216.
79. K. Hamada, F.Kawano, and K.Asaoka, Shape recovery of shape memory alloy fiber embedded resin matrix smart composite after crack repair, Dent. Mater. J., 22(2003) 160–167.

*****