Autonomic Healing of Polymers

Scott R. White, Mary M. Caruso, and Jeffrey S. Moore

Abstract

Self-healing polymers have experienced rapid technological advancement over the past seven years. They have moved from a conceptual demonstration to practical application in this time frame and have grown from a single design to a generic paradigm for modern materials development. Potential applications of self-healing polymers are quite broad, including microelectronic substrates and encapsulants, polymeric paints and coatings, structural composites, and biomedical devices. In this article, we focus on polymeric systems that heal in an autonomic fashion, that is, automatically and without human intervention. The types of systems under development and the future of this paradigm in advanced materials are discussed.

Introduction

One natural fate of engineered materials is a slow and steady degradation in performance throughout their service life. Degradation is often a complex mechanism involving many environmental factors that accelerates with time. For a new class of self-healing materials, this unrelenting march toward eventual material failure is no longer a certainty. Self-healing polymers exhibit the ability to repair themselves and recover functional performance using the resources inherently available to them. To trigger this repair, they might require some form of external activation (such as heat). A more restrictive class of self-healing materials achieves functional recovery in an autonomic fashion, that is, automatically and without human intervention.

The general concept of autonomic healing is depicted in Figure 1a. When damage occurs in the material, a crack forms and eventually propagates until it ruptures a microcapsule that contains a healing agent. The healing agent is then transported to the crack plane and undergoes polymerization, rebonding the crack faces. The entire process is triggered by damage, and recovery occurs under ambient conditions requiring no external source of energy (such as heat). Many different types of materials systems have been developed, but all are predicated on the same underlying concepts of healing through compartmentalization of reactive phases.

Microencapsulated Systems

Autonomic healing was first demonstrated in 2001 in a structural epoxy containing a microencapsulated healing agent and a suspended solid-phase catalyst.[1] This first demonstration utilized polymeric microcapsules containing a liquid monomer (dicyclopentadiene, DCPD) dispersed in a bisphenol A epoxide (Epon 828) cured with diethylenetriamine (DETA) curing agent. A solid-phase ring-opening metathesis polymerization (ROMP) catalyst (first-generation Grubbs catalyst) was dispersed in particulate form within the unreacted polymer matrix together with the microcapsules. (See the article by Williams et al. in this issue for ROMP reaction details.) After curing of the epoxy matrix, fracture experiments were performed for virgin and healed materials, and recovery of up to 70% of the virgin mode-I fracture toughness was demonstrated.

This motif of dispersing a microencapsulated healing agent has since been applied to multiple polymeric systems and proven to be a generic platform for achieving autonomic healing functionality. Three types of systems have been demonstrated (Figure 1b), all of which are triggered when damage occurs in the material and the strong stress singularity at the crack tip drives the crack forward until it ruptures a microcapsule. In the original autonomic self-healing system developed by White et al., the healing agent (monomer) was microencapsulated, and a solid catalyst was dispersed throughout the polymer matrix (Figure 1b, left).[1] Alternatively, both phases can be encapsulated and dispersed (Figure 1b, center),[2] or the healing agent can be phase-separated in the matrix (Figure 1b, right).[3] The desired healing chemistry and polymer matrix in which the healing will occur dictate the specific type of system used. For example, if chemical reactions are possible between the polymer matrix and either phase of the healing chemistry, the dual-capsule approach ensures that healing reactions occur only after the material incurs damage.

Assessment of healing in structural materials is based on mechanical performance recovery (Figure 1c). The initial (virgin) and healed responses of a material are measured following experimental protocols that are specific to the performance metric of interest. For example, the tapered double cantilever beam (TDCB) sample geometry provides a crack-length-independent measure of fracture toughness (K_{IC}) and the ratio of healed to virgin toughness is a common measure of healing efficiency (η). Other definitions of healing efficiency can be used that are coupled to other specific performance metrics (e.g., stiffness, ultimate strength). Further development of self-healing epoxy has led to increased healing efficiency,[4] reduced catalyst concentration,[2] alternative catalysts,[5] reduced microcapsule size,[6,7] faster healing kinetics,[8,9] and healing under dynamic loading conditions[10–12] (Figure 2).

Dynamic (fatigue) healing is an important example that highlights the interplay between the kinetic processes that are operative during the healing process (Figure 3). During fatigue, the crack tip propagates at a particular kinetic rate that is largely dictated by the mechanical environment (frequency, stress amplitude, and so on). In opposition to this, healing occurs at some other kinetic rate that accounts for characteristic times needed for rupture of the microcapsules, transport of the healing agent, mixing with the catalyst, and initiation and polymerization of the healing agent.

Of these healing processes, the polymerization stage is largely dominant under normal conditions. When mechanical kinetics dominates, damage accumulates so quickly that there is not sufficient time for healing to mitigate, and degradation in the material proceeds largely unimpeded. Conversely, when healing kinetics dominates, then damage proceeds so slowly that it is immediately suppressed and fatigue cracks can be permanently arrested, thereby imparting what appears

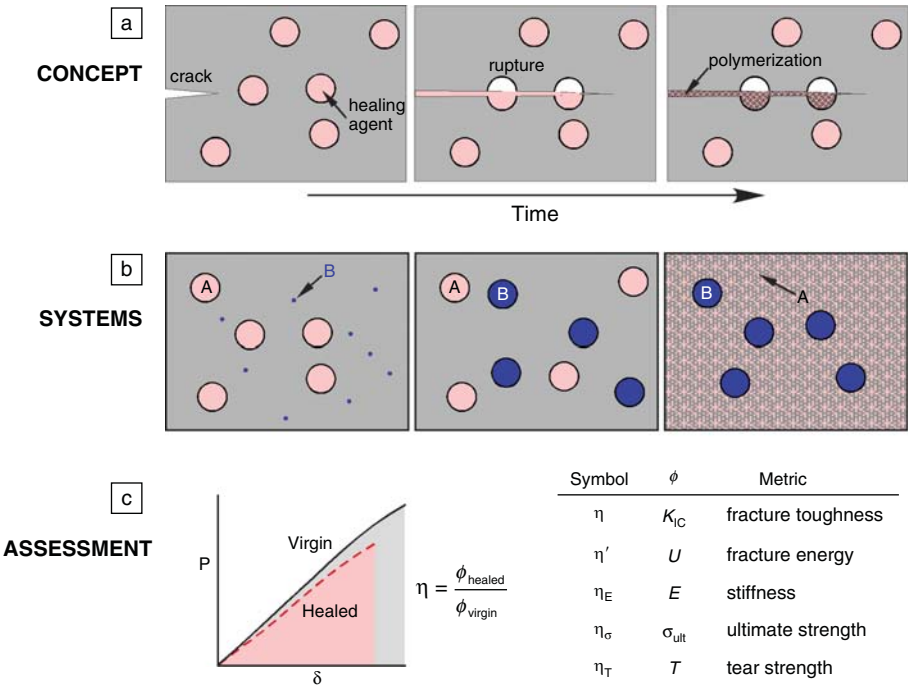

Figure 1. Autonomic healing of polymers. (a) Underlying concept in which damage (a crack) triggers the healing response by rupturing embedded microcapsules containing a healing agent that polymerizes in the crack plane, rebonding crack faces. (b) Types of autonomic healing systems: (left) the healing agent (A) is encapsulated, and the catalyst (B) is dispersed in the polymer matrix; (center) both the healing agent and catalyst phases are microencapsulated and dispersed in the matrix; (right) the healing agent is phase-separated in the matrix, and the catalyst phase is microencapsulated. (c) Assessment of healing efficiency (η) is based on the recovery of mechanical properties of interest including fracture toughness, fracture energy, stiffness, ultimate strength, and tear strength. P is load; δ is displacement.

to be a fatigue threshold in self-healing epoxy.[12] The ultimate challenge is to engineer systems in which the rate of damage accumulation is exactly balanced by the rate of healing so that the material systems remain in a stable configuration.

Other polymeric systems have incorporated microencapsulated healing agents and shown self-healing capability. A self-healing vinyl ester has been demonstrated using the same microencapsulated ROMP healing chemistry,[13] as well as a poly(dimethylsiloxane)- (PDMS-) based chemistry.[3] In the latter case, the healing agent is phase-separated in the matrix (vinyl ester), and the catalyst is dispersed through polymeric microcapsules. The appeal of PDMS-based healing chemistries is their tolerance for humid or wet environments, their stability to elevated service temperatures, and the cost effectiveness of the component materials. Because the polymerized healing agent is elastomeric, its load-carrying capability is not optimal, but the ability to seal cracks might find beneficial practical applications.

A self-healing elastomer matrix was recently demonstrated that used dispersed microcapsules containing a two-part PDMS hydrosilylation reaction system.[14] The healing mechanism follows the same motif of microcapsule rupture followed by healing-agent transport, mixing, initiation, and polymerization in the crack plane. In Keller et al.'s demonstration, the healing chemistry and the matrix chemistry are analogous. As such, chemical compatibility of the healing agent and matrix polymer are perfect, and in many cases, 100% recovery of tear strength was obtained.[14]

Microcapsules containing a material that forms films have also been evaluated for use in epoxy paints.[15] Microencapsulated tung oil and spar varnish were introduced into a commercial epoxy primer, which was then top coated with an epoxy paint[15] and subjected to surface damage. Upon exposure to corrosive environments, undercutting of the surface damage was measured and found to be inhibited by the self-healing functionality.

For all microencapsulated systems reported to date, there still exist technical challenges in realizing their practical application for microelectronic substrates and encapsulants, polymeric paints and coatings, structural composites, and biomedical devices. In some cases, the cost of healing components is high; in others, the concern is environmental stability or toxicity. Manufacturing integration, dispersion of phases, and kinetic rates of healing are active areas of development in self-healing research. With the recent introduction of solvent-based healing systems,[16] a cost-effective and practical realization of autonomic healing is now within site. In this elegant approach, a solvent of optimal polarity is delivered to the crack plane through rupture and release from embedded microcapsules. Two mechanisms of healing likely contribute to over 80% recovery of virgin fracture toughness.[16] Upon delivery of the solvent to the crack plane, the mobility of reactive phases local to the site of damage is increased, and formation of new chemical bonds can occur, as can increased chain entanglement across the crack plane. A wide range of solvents have been shown to work for epoxies and could potentially be extended to thermoplastic systems as well.[16]

To date, the only autonomic healing system that does not follow the microcapsule motif is the intriguing approach of hybrid polymer gels that contain reversible metal–ligand complexes.[17] Although reversible noncovalent interactions have been suggested as a route to endow materials with self-healing properties, their utility as a structural polymer is not obvious. Yet, both structural and healing functionalities can potentially be realized simultaneously by creating a hybrid (composite) polymer. Overall structural function is satisfied in this approach by creating a covalently bonded polymer network scaffold. By grafting side-chain ligands onto this polymer network, healing is accomplished through reversible metal–ligand complexes between these polymer side-chain ligands and coordinating metal complexes.

Microvascular Systems

The future of self-healing polymers will see continued progress in autonomic systems following the conceptual approaches just outlined, including practical applications and commercial development across many industrial markets. Two important recent breakthroughs in the field will greatly expand the types of materials that can self-heal, the types of chemistries that can be used, and the long-term performance of self-healing polymers.

For any self-healing polymer that relies on a reservoir of healing components stored within the material, only a limited supply of these components is carried

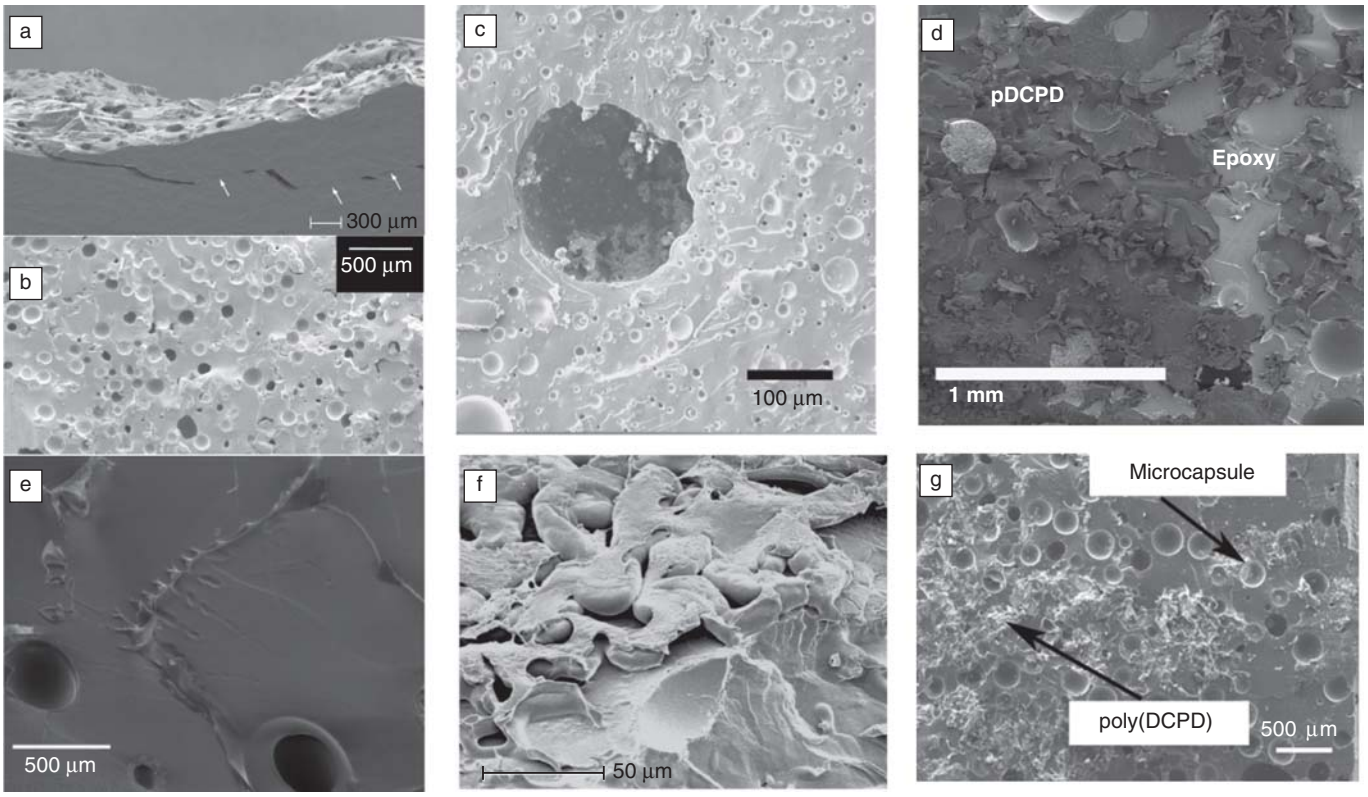

Figure 2. Autonomic healing polymers. (a) Poly(dimethylsiloxane) (PDMS) matrix healed with two-part PDMS resin and initiator capsules.[14] (b) Epoxy matrix healed through microencapsulated solvents.[16] (c) Vinyl ester matrix healed with phase-separated PDMS and organotin-containing microcapsules.[3] (d) Epoxy matrix healed with dicyclopentadiene (DCPD) capsules and wax-encapsulated Grubbs catalyst.[6] (e) Epoxy matrix healed by DCPD capsules and Grubbs catalyst.[1] (f) Epoxy matrix healed under dynamic loading conditions by DCPD microcapsule and Grubbs catalyst.[11] (g) Epoxy matrix healed with DCPD capsules and tungsten hexachloride catalyst.[5]

with the material throughout its lifetime. At some point in the future, once the resources have been consumed, the material will no longer function as intended unless the material can be resupplied with healing components. Nature's answer to the issue of limited resources is a circulatory network that continually resupplies nutrients and other functional components to the host organism. The first evidence of microvascular-/circulatory-based healing polymers was recently demonstrated[18] in which a single crack was repeatedly healed up to seven successive times through resupply of healing agent from a microvascular substrate (Figure 4). No warpage was involved, and the material recovered structural integrity and fracture toughness. Other approaches using entropically driven nanoparticle segregation in cracks supplied through a vascular supply network have also been discussed.[19,20] These microvascular-based approaches will lead to self-healing polymers with vastly extended lifetimes and the ability to heal macroscopic damage in which large volumes of healing components are required for delivery to the site of damage.

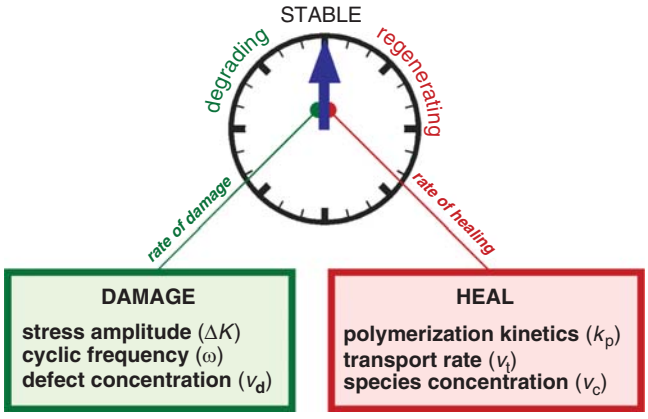

Figure 3. Dynamic healing of polymers. For optimal performance, the rate of healing must be closely matched to the rate of damage accumulation so that a stable material state is maintained.

With the recent report of the coupling of mechanical force directly to chemical reactions through mechanophores,[21] the opportunity to develop completely new structural polymers for self-healing has emerged. With rational mechanophore design and integration into structural polymers, such materials will now be able to actively and productively respond to mechanical force. Reconfiguring bonds to

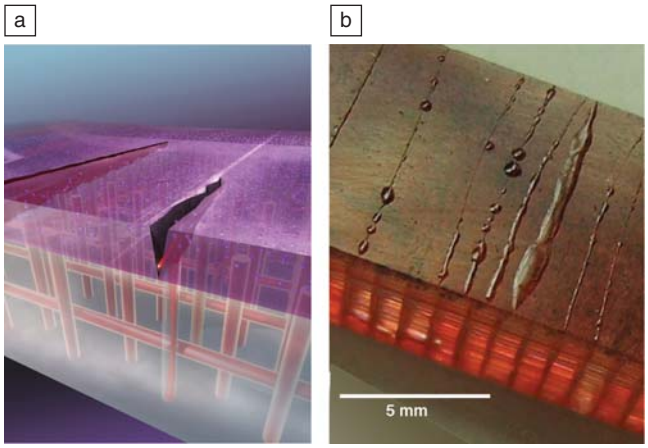

Figure 4. Microvascular-based healing of polymers: (a) interconnected microchannels in the substrate contain a supply of healing agent (red) that fills surface cracks in a self-healing coating (purple), (b) microvascular self-healing epoxy sample containing Grubbs catalyst in the coating layer and showing excess healing agent (dicyclopentadiene, DCPD) released on the surface of the sample after transverse cracks were introduced in four-point bend testing.

absorb imposed (excessive) deformation, locally cross-linking to prevent crack propagation, and changing color signature[22] to indicate overload conditions are just a few of the concepts that will emerge in the future.

Summary

Self-healing polymers have rapidly become an important research focus in materials science and engineering. Their emergence in the past decade creates new opportunities in polymers and composites for engineering systems that are maintenance-free, long-lived, more robust, and safe. Most of the autonomic systems described here involve the incorporation of compartmentalized liquids into polymeric materials. Damage triggers the local release of this liquid, causing subsequent healing through a combination of mass transport and chemical changes. Quite remarkably, these materials appear to "bleed" in the regions that experience damage. Intuitively, the thought of adding liquid components to polymeric materials, especially structural resins, runs counter to conventional wisdom. However, not only can micrometer-sized liquid-filled compartments offer healing capability, they have also been shown to be effective toughening agents.[23]

The small reduction in strength and stiffness that accompanies the addition of microcapsules is offset by the benefits of new self-healing (and potentially other) functions. The notion of bleeding materials brought about by the addition of liquid components to solid polymers is an entirely new paradigm in materials research, the potential of which has yet to be fully realized. We have attempted to provide an overview of the growing number of approaches that have been demonstrated in self-healing polymers and to project where new developments in the field will occur in the near future.

Acknowledgments

Financial support from the Air Force Office of Scientific Research is gratefully acknowledged.

References

1. S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan, *Nature* **409**, 794 (2001).
2. J.D. Rule, E.N. Brown, N.R. Sottos, S.R. White, J.S. Moore, *Adv. Mater*. **17**, 205 (2005).
3. S.H. Cho, H.M. Andersson, S.R. White, N.R. Sottos, P.V. Braun, *Adv. Mater*. **18**, 997 (2006).
4. E.N. Brown, N.R. Sottos, S.R. White, *Exp. Mech*. **42**, 372 (2002).
5. J.M. Kamphaus, J.D. Rule, J.S. Moore, N.R. Sottos, S.R. White, *J. R. Soc. Interface* **5**, 95 (2008).
6. J.D. Rule, N.R. Sottos, S.R. White, *Polymer* **48**, 3520 (2007).
7. B.J. Blaiszik, N.R. Sottos, S.R. White, *Compos. Sci. Technol*. **68**, 978 (2008).
8. A.S. Jones, J.D. Rule, J.S. Moore, S.R. White, N.R. Sottos, *Chem. Mater*. **18**, 1312 (2006).
9. T.C. Mauldin, J.D. Rule, N.R. Sottos, S.R. White, J.S. Moore, *J. R. Soc. Interface* **4**, 389 (2007).
10. E.N. Brown, S.R. White, N.R. Sottos, *Compos. Sci. Technol*. **65**, 2466 (2005).
11. E.N. Brown, S.R. White, N.R. Sottos, *Compos. Sci. Technol*. **65**, 2474 (2005).
12. A.S. Jones, J.D. Rule, J.S. Moore, N.R. Sottos, S.R. White, *J. R. Soc. Interface* **4**, 395 (2007).
13. G.O. Wilson, J.S. Moore, S.R. White, N.R. Sottos, H.M. Andersson, *Adv. Funct. Mater*. **18**, 44 (2008).
14. M.W. Keller, S.R. White, N.R. Sottos, *Adv. Funct. Mater*. **17**, 2399 (2007).
15. A. Kumar, L.D. Stephenson, J.N. Murray, *Prog. Org. Coat*. **55**, 244 (2006).
16. M.M. Caruso, D.A. Delafuente, V. Ho, N.R. Sottos, J.S. Moore, S.R. White, *Macromolecules* **40**, 8830 (2007).
17. F.R. Kersey, D.M. Loveless, S.L. Craig, *J. R. Soc. Interface* **4**, 373 (2007).
18. K.S. Toohey, N.R. Sottos, J.A. Lewis, J.S. Moore, S.R. White, *Nat. Mater*. **6**, 581 (2007).
19. J.Y. Lee, G.A. Buxton, A.C. Balazs, *J. Chem. Phys*. **121**, 5531 (2004).
20. S. Gupta, Q. Zhang, T. Emrick, A.C. Balazs, T.P. Russell, *Nat. Mater*. **5**, 229 (2006).
21. C.R. Hickenboth, J.S. Moore, S.R. White, N.R. Sottos, J. Baudry, S.R. Wilson, *Nature* **446**, 423 (2007).
22. S.L. Potisek, D.A. Davis, N.R. Sottos, S.R. White, J.S. Moore, *J. Am. Chem. Soc*. **129**, 13808 (2007).
23. E.N. Brown, S.R. White, N.R. Sottos, *J. Mater. Sci*. **39**, 1703 (2004). □