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ENRICHMENT OF SELF-HEALING MATERIAL AND ADVANCED COMPOSITE STRUCTURES

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ABSTRACT

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Self-healing material is taking an increase number of interest worldwide because of their autonomic healing properties. This unique material behavior is inspired by biological systems. In this study different approaches for self-healing materials are shown. Three conceptual approaches are available for self-healing: capsule-based healing systems, vascular healing systems, and intrinsic healing polymers. This article reviews about the self-healing process of composite material using microcapsule and hollow fiber. Influence of microcapsule content on tensile performance is also reviewed and found better for advanced composite structure.

Key words: *self-healing, microcapsule, composite and fibre*

INTRODUCTION

Improvements of many engineering structures and major performances largely depends on advances in materials technologies and continue to be key in determining the reliability, performance and cost effectiveness of such systems. Continuous improvement of structures is a common feature for engineering structures. Engineering structures now embrace a wide range of technologies from materials development, analysis, design, testing, production and maintenance (Williams *et al.* 2006). Engineering research has been focused usually on either the design of new materials with increased robustness or the development of nondestructive evaluation methods for material inspection. Lightweight, high strength, high stiffness reinforced polymer composite materials are leading contenders as component materials to improve the efficiency and sustainability. Furthermore, they offer immense scope including multifunctionality due to their hierarchical internal architecture (Rule *et al.* 2005).

Since the damages inside the materials are difficult to be perceived and to be repaired, in particular, the materials need to have the ability of self-healing. In fact, many naturally occurring materials in animals and plants are themselves self-healing materials. Accordingly, efforts have been made to mimic the natural healing in living bodies and to integrate the bio inspired self-healing capability into polymers and polymer composites. The progress in this aspect has opened an era of new intelligent materials. The basic idea for self healing comes from biological systems (Blaiszik *et al.* 2001). Composite material with self healing monomer has the ability to repair the structure automatically using the resources inherently available to them. This damage often manifests itself on the inside within the material as matrix cracks and delaminations, and can thus be difficult to detect visually. Thus, a polymer composite with capsule material could directly benefit from incorporating an added functionality such as self-healing. Self-healing materials offer a new way toward longer-lasting products, safer and components (Hucker *et al.* 1999).

MATERIALS AND METHODS

Approaches to self-healing materials

Self-healing is defined as the capability of a material to heal (recover/repair) damages automatically and autonomously, that is, without any external intervention (Ghosh and kumar, 2009). Different common terms are used to describe the self healing properties of material such as self repairing, autonomous healing and automatic repairing. Self healing can be broadly classified as three groups' capsule based, vascular, and intrinsic (Fig: 2.1). Each approach differ with each other depend on the mechanism of healing functionality. Recovery rate of damage portion for different strategies are different because of different structural difference.

Release of healing agent is possible with different process. Microcapsule embedment is one which is commonly used for releasing healing agent. Capsule based self healing composite (Fig: 1a) contain the healing agent inside the capsule. When the capsules are cracked by damage, the self-healing mechanism is triggered through the release and reaction of the healing agent in the region of damage. After release, the local healing agent is depleted, leading to only a singular local healing event.

Releasing of the healing agent for vascular self-healing materials (Fig: 2.1b) in the form of hollow channels, which may be interconnected in different dimension example: one-dimensionally (1D), two-dimensionally (2D), or three-dimensionally (3D), until damage triggers self-healing (Larin *et al.* 2006). Damage initiate the releasing of healing agent from the hollow channel, 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.

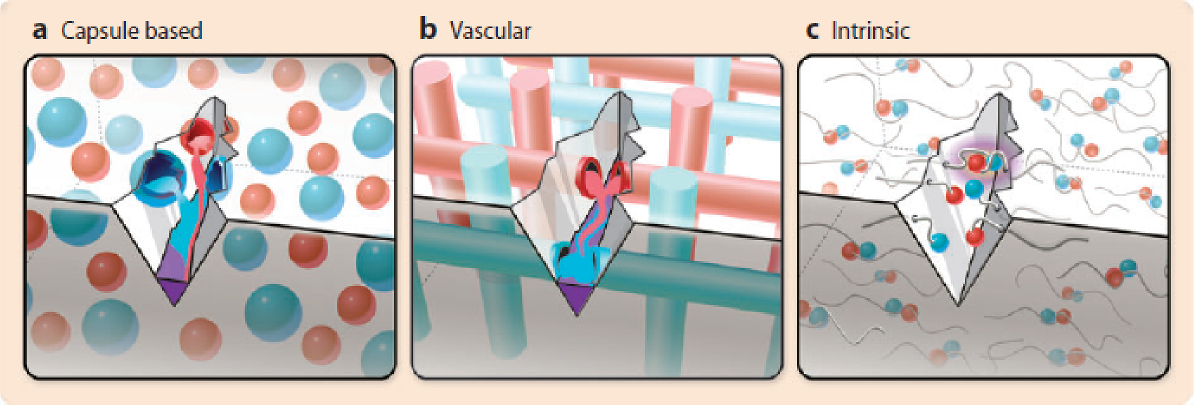

Figure: 2.1 Approaches to self-healing include (*a*) capsule-based, (*b*) vascular, and (*c*) intrinsic methods. Each approach differs according to the method by which healing functionality is integrated into the bulk material. (*a*) In capsule-based self-healing materials, the healing agents stored in capsules until they are ruptured by damage or dissolved. (*b*) For vascular materials, the healing agent is stored in hollow channels or fibers until damage ruptures the vasculature and releases the healing agent. (*c*) Intrinsic materials contain a latent functionality that triggers self-healing of damage via thermally reversible reactions, hydrogen bonding, ionomeric arrangements, or molecular diffusion and entanglement. Shades of red and blue are used in this figure and throughout the review to show a generalized interaction (purple) between two or more species.

Self-healing materials with intrinsic method (Figure 2.1*c*) do not release healing agent but has the properties of latent self-healing functionality that is triggered by damage or by an external stimulus. These materials depend on chain mobility and entanglement, reversible polymerizations, melting of thermoplastic phases, hydrogen bonding, or ionic interactions to initiate self-healing. Because each of these reactions is reversible, multiple healing events are possible.

Capsule based self-healing material

Capsule based self healing composite material consists of micron sized bubbles or microcapsules filled with self healing monomer. Microencapsulation is a method of enclosing micron-sized elements of solids, droplets of liquids, or gases in an inert shell, which in turn isolates and protects them from the external environments. The end product of the microencapsulation process is termed as microcapsules. It has two parts, namely, the core and the shell. They may have spherical or irregular shapes and may vary in size ranging from nano-to micro scale. Healing agents or catalysts containing microcapsules are used to design self-healing polymer composites. The first practical demonstration of self-healing materials was performed in 2001 by Prof. Scot White and his collaborators (Patel *et al.* 2010). Self-healing capabilities were achieved by embedding encapsulated healing agents into polymer matrix containing dispersed catalysts. The self-healing strategy used by them is shown in Fig: 2.2.

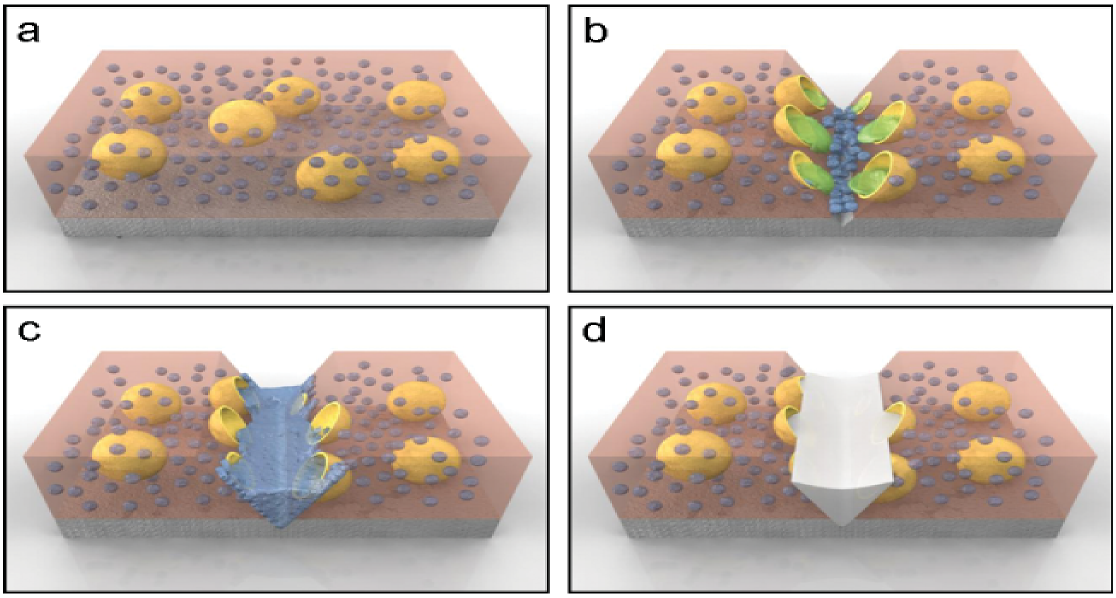

Figure 2.2 Schematic of self-healing process. a) Self-healing coating containing microencapsulated catalyst (yellow) and phase-separated healing agent droplets (blue) in a matrix (light orange) on a metallic substrate (grey). b) Damage to the coating layer releases catalyst (green) and healing agent (blue). c) Mixing of healing agent and catalyst in the damaged region. d) Damage healed by cross-linked, protecting the substrate from the environment (Soo *et al.* 2007).

Dicyclopentadiene (DCPD) as the liquid healing agent and Grubbs' catalyst [bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride] as an internal chemical trigger and dispersed them in an epoxy matrix. The monomer is relatively less expensive and has high longevity and low viscosity. Fig: 1.2 shows a representative morphology of encapsulated DCPD and Grubb's catalyst.

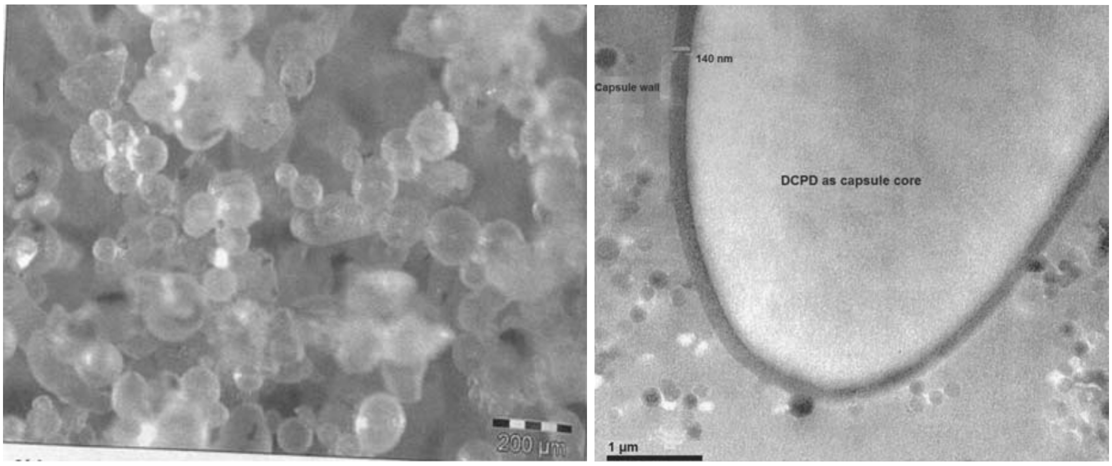

Fig. 1.2 Light microscopic picture of encapsulated DCPD and Grubb's catalyst

When DCPD comes into contact with the Grubbs' catalyst dispersed in the epoxy resin a Ring Opening Metathesis Polymerization (ROMP) (Rule and Moore, 2002; Brown *et al.* 2004) starts and a highly cross-linked tough polycyclopendiene is formed that seals the crack (Fig: 2.3).

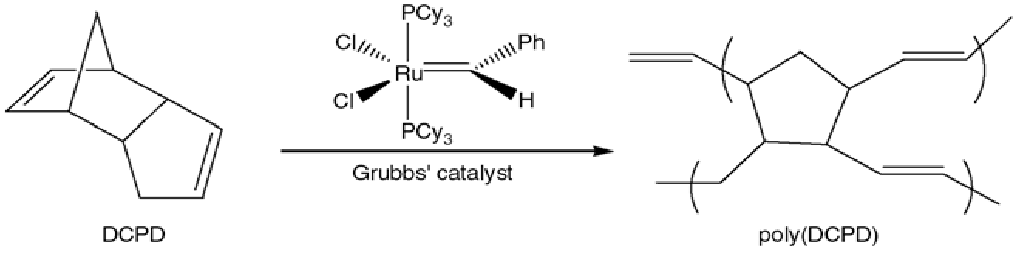

Fig. 2.3 Ring opening metathesis polymerization of DCPD

Tensile performance of self-healing epoxy

Since the microencapsulated epoxy and the latent curing agent must be filled into the composites' matrix, it is worth understanding their influence on the basic mechanical performance of the matrix. Hence, tensile properties of epoxy containing the self-repair system were measured as a function of the microcapsules' concentration at a fixed content of $CuBr_2$(2-MeIm)4.

The plots in Figure 2.5a exhibit that tensile strength of the compounds is retained almost unchanged with a rise in the content of the microcapsules. It is different from the results of Brown *et al.* (2004) who reported a continuous reduction in the strength of epoxy with embedded microcapsules. The strength data in Figure 2.5a suggest that the shell material of the microcapsules, urea-formaldehyde resin, is compatible with epoxy and a strong interfacial interaction was established during curing. Moreover, unlike the soft rubber, the microcapsules are able to carry certain load transferred by the interface. These accounts for the dependence of tensile strength on the content of microcapsules illustrated in Fig: 2.5(a).

On the other hand, the increase in failure strain (Fig: 2.5b) should be attributed to the fact that the microcapsules have induced interfacial viscoelastic deformation and matrix yielding. The decrease in elongation at break for the highly loaded specimens might be due to the uneven distribution of the microcapsules, which led to stress concentration in some parts of the specimen.

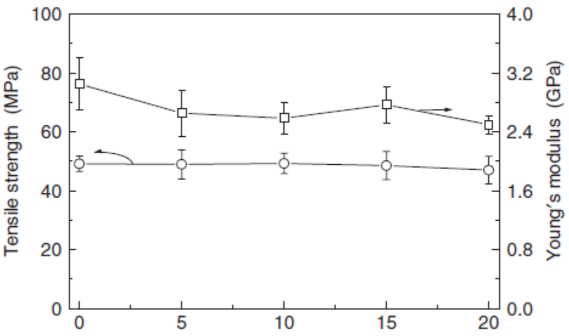

Fig. 2.5(a) Influence of microcapsules content on tensile strength

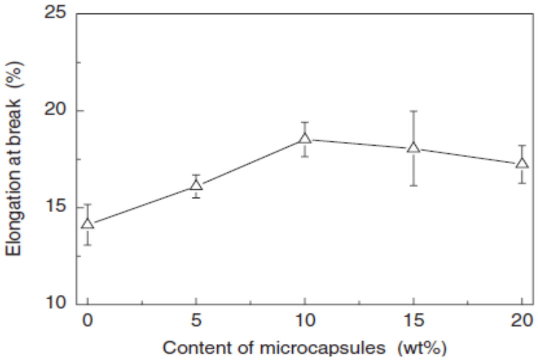

Fig. 2.5(b) Influence of microcapsules content on elongation at break

Hollow fiber embedment

Microcapsule-based self-healing approach has the major disadvantage of uncertainty in achieving complete and/or multiple healing as it has limited amount of healing agent. Multiple healing is only feasible when excess healing agent is available in the matrix after the first healing has occurred. Thus, to achieve multiple healing in composite materials, another type of reservoir that might be able to deliver large amount of liquid healing agent was developed by Dry and coworkers (Dry 1996; Dry 1995). Bond and coworkers later developed a process to optimize the production of hollow glass fibers (Trask and Bond, 2006) and used these fibers as the container for liquid healing agents and/or dyes (Pang and Bond, 2005). These borosilicate glass fibers' have diameter ranging from 30 to 100 µm with hollowness of 55%.

They have demonstrated that composite panels prepared using hollow fibers containing repairing agents can restore up to 97% of its initial flexural strength. The release and infiltration of fluorescent dye from fractured hollow fibers into the crack plane was also demonstrated. This approach of self-healing material design offers certain advantages, which are as follows:

- Higher volume of healing agent is available to repair damage;
- Different activation methods/types of resin can be used;
- Visual inspection of the damaged site is feasible;
- Hollow fibers can easily be mixed and tailored with the conventional reinforcing fibers.

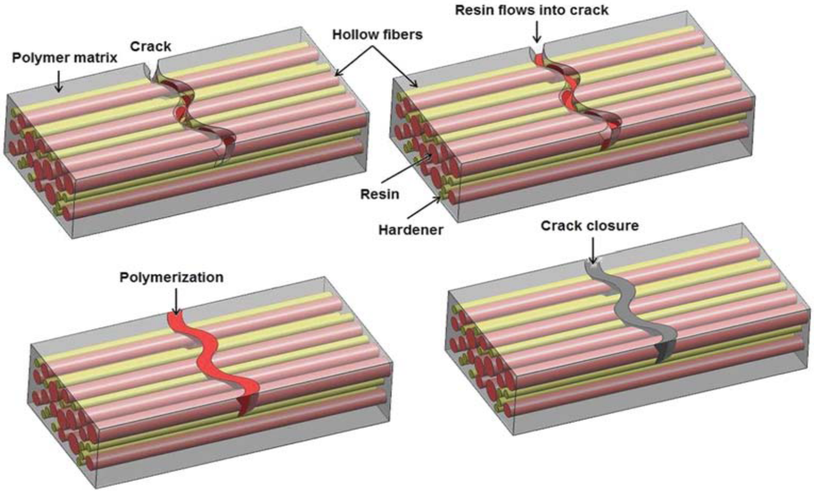

Fig. 2.6 Schematic representation of self-healing concept using hollow fibers

Application area for composite material

Self-healing materials development is either in the preliminary or product level, and so these materials are yet to be available for many applications. Applications of self-healing materials are expected almost entirely in all industries in future. The very few applications being developed to date 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 (Larin *et al.* 2006). The self-healing paint, currently applied to certain Nissan and Infiniti vehicles worldwide, was developed in collaboration with University of Tokyo and Advanced Soft materials Inc. (Dry 1995).

Wherever materials are used, self-healing concepts may lead to enhanced utility. Longer life, safer self-healing batteries, resealing tires, fade-resistant fabrics, and ant tamper electronics are all potential applications for self-healing concepts Application areas for textile composites are primarily within the aerospace, marine, defense, land transportation, construction and power generation sectors (White *et al.* 2001). Self-healing polymers embedded into the textile reinforce polymer composite are used for defense application. Self-healing smart fibers are used in building reinforced concrete as a crack management technology.

These polymer composite offer high potential with long lived structural material. In the near future self healing coating for textiles will become a hot issue in the textile industry. Self-healing coating is introduced to protect the underlying textile substrate. But the challenges are to find the appropriate microcapsules for the specific applications (Dubey *et al.* 2009).

CONCLUSION

This nascent field of research has made great paces over the past several years, but many technical challenges remain, and there exists an immense need for focused research efforts to address several areas of concern. Self-healing aims will most likely demand targeted and localized distribution of self-healing components in large-scale applications to maximize efficiency while minimizing cost and harmful effects to the matrix material. To be able to build up new innovative solutions based on biomimetic approaches, it is an ultimate need to conquer the difficulties of damage detection and attaining an autonomic-healing phenomenon. Besides autonomic-healing, nonautonomic practices will also find industrial applications. It is sure that this wonderful field of self-healing materials will continue to grow beyond the technologies reviewed here and it will become available for our daily uses.

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