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Feature Article

Effect of polymer architecture on the intrinsic self-healing character of polymers

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ABSTRACT

Intrinsic and extrinsic self-healing strategies can be employed to mitigate the effects of local damage in order to (partially) restore a lost property or functionality and to avoid premature catastrophic failure of the whole system.

It is well known that polymer architecture has a crucial influence on mechanical, physical and thermal properties. However, the effect of polymer architecture on the healing capabilities of self-healing polymers has not yet been studied in detail. This paper addresses the effect of polymer architecture on the intrinsic healing character of polymeric materials using different reversible chemistries and aims at highlighting the need for more studies on this particular topic.

Contents

1. Introduction

Probably the most extreme case of natural self-healing or natural regeneration is the one observed in *Hydra*. *Hydra* are fresh-water polyps capable of regenerating a totally new individual from small pieces of the original polyp by a mechanism known as morphallaxis, i.e. regeneration occurring in the absence of cellular proliferation and involving the transformation of existing body parts or tissues into newly organized structures [1]. Unfortunately, engineered self-healing systems are still far away from this

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extreme and not fully understood type of healing. However, the generic principles that govern the healing of *Hydra* can still be applied to intrinsic healing polymers. While *Hydra* require delay time, reorganization of tissue, continuous signalling, gradients of molecule concentration to provide positional information, adhesion of regenerating cells to permanent wall, and critical minimum tissue size a healing polymer requires damage detection, resting time, reorganization of chains, polymer integrity maintained during healing, and critical damage size. Despite these similarities with *Hydra*, self-healing engineering systems have reached a level of development that allows more straight forward conceptual comparisons with the healing mechanisms used by other natural systems such as plants. In order to implement repair of large scale damages, plants follow a two-step repair process consisting of self-sealing by liquid flooding and self-healing by hardening of the released liquid. This two-step model forms the basis for extrinsic self-healing approaches where the healing agent (generally liquid) is incorporated into the matrix as discrete entities such as capsules, natural systems can still be used as an inspiration to develop intrinsic self-healing systems [2]. In the case of intrinsic healing approaches, where the healing capability is intrinsically connected to the (chemically or compositionally tuned) matrix polymer architecture, the two-step process can be translated into a softening step leading to local mobility towards the damage followed by a hardening process leading to the restoration of the original properties as represented in Fig. 1 by the recovery of the local viscosity after the healing trigger (temperature) is removed.

While intentionally created self-healing behavior has become an active research topic in materials science in recent years examples of pseudo-engineered systems have been available since the appearance of natural building materials such as adobe and mortar around 4–5000 years ago. In these basic construction materials the healing process occurs due to sequential dissolution and re-precipitation of matter at micro-cracks promoted by cyclic changes in ambient humidity. Following the landmark works of Dry and White [3,4] the concept of self-healing has been implemented into all classes of engineering materials [5–8] leading to different development stages depending on the material and the application field. For instance, self-healing asphalt by induction heating [9] and self-healing concrete by bacteria [10] are already at a pre-commercialization level while self-healing metals [11,12] are still at their very infancy.

The research on engineered healing systems initially aimed at the recovery of mechanical properties after a drastic failure [4] but the field has evolved towards the healing of a broader spectrum of damage types and sizes [7]. Other functionalities potentially healable can be as diverse as color, hardness, adhesion, corrosion protection, brightness, hydrophobicity, wear resistance, reflectivity, electrical or thermal conductivity, stealth, ion selection, and liquid or gas barrier.

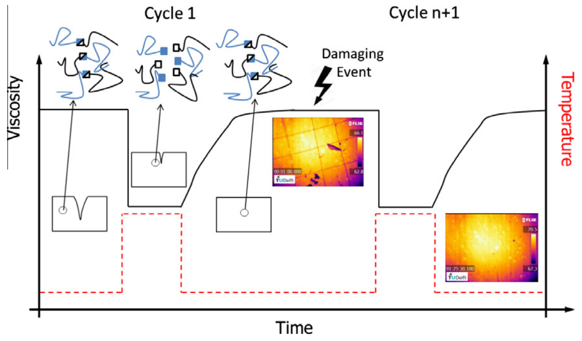

Fig. 1. General concept of matrix healing using intrinsic healing concepts. Figure shows a sudden drop in viscosity upon heating linked to local temporary network mobility necessary for flow and damage repair. Upon cooling the local properties (e.g. viscosity) are restored to initial values so the material can be further used. Figure also shows the multiple healing events possible with intrinsic healing concepts.

The field of self-healing is thus aiming at the restoration of a lost functionality (property) of a certain material in a specific application in order to extend the service lifetime of the whole system. Fig. 2 shows a schematic of the basic principle of lifetime extension by the implementation of healing concepts [13]. A traditional approach towards longer use of structures and systems is the development of more resistant and better materials than the original ones (curves a and b in Fig. 2). In the case of polymers, this is traditionally achieved by modifying the polymer architecture itself (e.g. crosslinking density, aromatic chains, crystallinity) or by introducing external agents such as exfoliated clays or graphene plates. While the traditional strategy of improving the initial properties leads to small developments due to the big advances reached so far, healing concepts offer an alternative strategy based on damage management rather than damage tolerance [5]. This new approach already led to very significant results despite the young age of the field. Curve c in Fig. 2 depicts an increase of service lifetime using one of the simplest self-healing approaches in which the initial properties have been partially recovered after damage. The most extreme case of lifetime extension would be one that allows multiple healing events with no loss of initial properties such as the one depicted in curve d in Fig. 2. Some polymeric systems capable of multiple healing events have already been developed [14,15] but the initial mechanical properties of these systems are far below those required in most of the

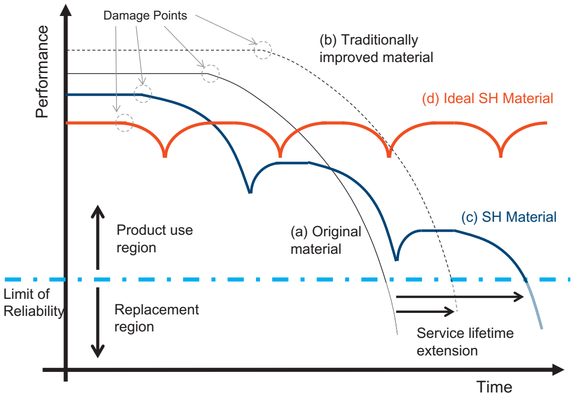

Fig. 2. Lifetime extension of engineered materials by implementation of self-healing principle.