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Review

Self-healing materials: A review of advances in materials, evaluation, characterization and monitoring techniques

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ABSTRACT

Self-healing materials are attracting increasing interest of the research community, over the last decades, due to their efficiency in detecting and "autonomically" healing damage. Numerous attempts are being presented every year focusing on the development of different self-healing systems as well as their integration to large scale production with the best possible property–cost relationship. The current work aims to present the most recent breakthroughs in these attempts from many different research groups published during the last five years. The current review focuses in polymeric systems and their composites. The reviewed literature is presented in three distinct categories, based on three different scopes of interest. These categories are (i) the materials and systems employed, (ii) the experimental techniques for the evaluation of materials properties and self-healing efficiency of the materials/structures and (iii) the characterization techniques utilized in order to evaluate (off-line) and monitor (on-line) the healing efficiency of the proposed systems. Published works are presented separately in all the different categories, thus the interested reader is advised to follow the structure of the review and refer to the chapter of interest.

1. Introduction

Self-healing materials are a relatively new class of smart materials that possess the ability to fully or partially recover a functionality that is mediated by operational use. Local functionality loss can be defined as the situation when a section of a material or structure exhibits degraded performance when compared with the rest of the material/structure. Global functionality loss can be defined as the situation when the material or structure exhibits degraded performance when compared to its properties prior to any exposure to operational loads.

This work focuses on self-healing polymers and their composites. The incorporation of healing agents in polymeric materials inadvertently leads in a new material with altered properties when compared to the material that does not possess the healing functionality. The performance and life-time of the new composite in conjunction with the efficiency of the self-healing functionality are of primary importance as they are often competing with each other.

The scope of the first section of this work is to describe the three primary self-healing approaches (intrinsic, capsule based and vascular) as well as the critical issues and challenges associated with each approach. A review of the literature on the materials that have been used as healing agents over the last five years is presented.

The aim of the second section of this review is to present the most frequently used testing procedures and specimen geometries found in research publications during the last five years. Special consideration is given to the ones that provide, either qualitatively or quantitatively, insight on the self-healing performance of the composites. Associated ASTM standards are also presented.

Finally, in order to gain an overall insight into the behavior of self-healing materials, their structure, performance and self-healing effectiveness is evaluated via the use of various characterization and monitoring techniques. The combination of mechanical testing and materials characterization techniques can exploit the actual capabilities as well as restraints associated with these materials. The ongoing development of the microscopic, spectroscopic and other characterization methods during the last decades, renders them invaluable tools, which can provide knowledge about the structure of materials, their chemical composition, as well as the way the react. In the last section of the current review, an extensive

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overview of the most common monitoring methods is presented. Typical microscopic methods such as optical and scanning electron microscopy as well as analytical and spectroscopic methods like NMR, AFM, FTIR and Raman spectroscopy employed for the evaluation and monitoring of self-healing are presented. The present review covers the literature published during the last five years, with more extensive information and paradigms in each different case.

2. Materials

The ability of self-healing materials to regain autonomously or externally assisted, their initial properties is primarily affected by the selection of the healing agents. Inspired by the biological systems, intrinsic, capsule-based and vascular methods, are the main approaches used in order to impart self-healing functionalities to materials or structures. A variety of self-healing agents have been extensively studied to meet the requirements of the new highly demanding applications of smart materials. This section is dedicated to the review of the research on the aforementioned three approaches as well as the materials that have been proposed as healing agents over the last five years.

2.1. Intrinsic self-healing materials

In the recent past, polymer science has reached at a point where it is possible to synthesize “smart” polymers that possess the remarkable, bio-inspired ability of regaining their initial properties completely, ideally without external input. These polymers constitute one of the most important categories of self-healing materials, that of the intrinsic or remendable healing polymers. In this case, repair is achieved through the inherent reversibility of bonding in the matrix phase, which acts as a healing agent.

Despite the good healing performance that was achieved in the first generation of intrinsic self-healing epoxy systems [1], the incorporation of dicyclopentadiene (DCPD)/Grubbs' catalyst within the matrix – an expensive and unstable in the hostile environment Grubbs' catalyst-limits its applications [2]. Within the aim of the research community is to maximize the healing efficiency and minimize the cost. Therefore, several other material and techniques have been developed in order to satisfy these criteria.

Thermally reversible reactions, especially the Diels–Alder (DA) reaction, for cross-linking linear polymers have been extensively studied by many researchers. Their main advantage is the theoretically infinite number of repetitions of the healing process without any further addition of chemical or healing agents [3–6]. Hermosilla et al. [7] presented a novel reversible thermoset polymer based on chemical modification of aliphatic polyketones into the corresponding derivatives containing furan and/or amine groups along the backbone. The furan moieties allow for the thermal setting of the polymer by the Diels–Alder (DA) and retro-DA sequence (bis-maleimide), while amine moieties allow for the tuning of the hydrogen bonding density. This new class of polymer material showed improved T_g values with respect to the respective counterparts containing only furan groups. Via this modification, these materials recover their mechanical properties after three thermal cycles. In another study, Joost Brancart et al. [8] investigated the ability of furan-maleimide building blocks to create reversible covenant networks in an epoxy based coating. Furan-fictionalized precursors were synthesized via reaction of amines with furfuryl glycidyl ether (FGE). The reversible cross-linking of the furan-precursors with a bis-maleimide was achieved in a two-step procedure. Thermal analysis of these composites showed that modification of the polymer network structure allows for the tailoring of the temperature for the self-healing process. Jenifer Ax and Gerhard Wenz [9] created a processible, remendable and highly oriented polymeric material with pending furane substituents, esterifying hydroxyethylcellulose with both furoyl chloride and acetic anhydride. In order to achieve crosslinking (DA reaction), 1,6-bis(N-maleimido)hexane was used. They have shown that both constituents can be mixed without premature formation of gels due to the low rate DA reaction under 70 °C. Yoshifumi Amamoto et al. [10] have successfully produced a cross-linked polymer based on reshuffling of thiuram disulfide (TDS) units. Stimulation of the self-healing process occurred under ambient conditions (visible light, air, room temperature) in the absence of a solvent. To carry out the self-healing reaction in a bulk material at room temperature, the reactive TDS units, capable of re-shuffling, were incorporated in the main chain of a low T_g polyurethane. In a more recent work, Claudio Toncelli and co-workers [11] presented the successful synthesis and crosslinking of functionalized (varying amounts of furan groups) polyketones with (methylene-di-p-phenylene)bis-maleimide. In addition, they managed to modify thermal and mechanical properties of the material by controlling the furan reactions. This self-healable polymer exhibited an almost full recovery of thermal and mechanical properties for seven consecutive self-healing cycles, independently of the furan intake. Guadalupe Rivero et al. [12] managed to produce polyurethane networks with healing capability, based on PCL and furan-maleimide chemistry, at mild temperature conditions via one-pot synthesis. A combination of a quick shape memory effect (contact of the free furan and maleimide moieties) followed by a progressive Diels–Alder reaction (reformation of the covenant bonds) allows the remendable process to take place at 50 °C, resulting in a complete recovery of the structural integrity without complete melting of the polymer. A schematic representation of the Diels–Alder based shape memory assisted self-healing process is depicted in Fig. 1.

A new approach for the development of self-healing nanocomposites was proposed by Sandra Schafer and Guido Kickelbick [13]. In their study surface-functionalized silica nanoparticles were used as cross-linking agents in thermally triggered self-healing

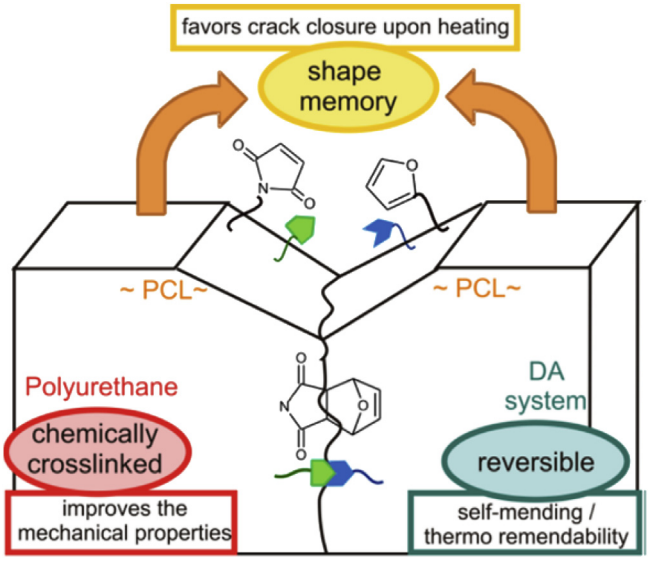

Fig. 1. Schematic depiction of the Diels–Alder based shape memory assisted self-healing process in a polyurethane material based on PCL and furan-maleimide chemistry [12].
Reprinted with permission from Rivero G, Nguyen L-TT, Hillewaere XKD, Du Prez FE. One-Pot Thermo-Remendable Shape Memory Polyurethanes. Macromolecules. 47(6):2010–8. Copyright (2014) American Chemical Society.