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Self-healing of densely crosslinked thermoset polymers—a critical review

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ABSTRACT

Structural and functional thermosetting composite materials are exposed to different kinds of stress which can damage the polymer matrix, thus impairing the intended properties. Therefore, self-healing materials have attracted the attention of many research groups over the last decades in order to provide satisfactory material properties and outstanding product durability. The present article provides a critical overview of promising self-healing strategies for crosslinked thermoset polymers. It is organized in two parts: an overview about the different approaches to self-healing is given in the first part, whereas the second part focuses on the specific chemistries of the main strategies to achieve self-healing through crosslinking. It is attempted to provide a comprehensive discussion of different approaches which are described in the scientific literature. By comparison of the advantages and disadvantages, the authors wish to provide helpful insights on the assessment of the potential to transfer the extensive present knowledge about self-healing materials and methods to surface varnishing thermoset coatings.

Contents

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1. Introduction

Polymer materials performance, lifetime, and safety are essential properties in many industries such as construction, automotive, aerospace, medical, furniture, etc. As such materials are usually exposed to certain environmental conditions (UV, scratches...) that can damage them, the integration of an ability to self-heal has become a technological challenge that can be beneficial to all these domains. Consequently, development of self-healing polymeric materials has been the topic of many studies over the last decades and many new self-healing systems and strategies for improving existing ones have been proposed to obtain a sustainable economy for long lasting applications. Self-healing increases the durability of thermosets by reducing the notch stress and in turn reduces the service costs for high end applications e.g. rotor blades in wind energy, turbines and aircraft or space craft applications. Unfortunately, the application of polymeric materials often raises the issue of a compromise between material performance and integration of self-healing properties. For instance, hard surface materials have specific properties (hardness, brightness, transparency, etc.) that are wished to remain unchanged both by the applied self-healing chemistry (no modification of standard surface polymer formulation) during use and the self-healing event after being triggered by a damaging influence (restoration of original surface performance). As such surfaces are usually made of highly crosslinked thermoset polymers, incorporating self-healing functionalities into their formulations can be problematic and needs to be investigated.

Material scientists have developed self-healing surface coatings [1] and successfully applied this concept to a wide range of materials and other technologies (e.g. [2,3]). Moreover, self-healing technologies are subjects in different sciences such as software engineering, micro-electro-mechanical systems, mechanics, self-reconfigurable robotics and electronics. The existing scale of the technology readiness level (TRL) [4] to assign different self-healing processes and materials to their implementation ability was used by Frei et al. and ranges from 1 to 9 [5]. Frei et al. reported classification of most applications in self-healing topics in classes 2 to 4. Nevertheless, in material sciences the TRL is at stage 4 (component and/or breadboard validation in laboratory environment) or 5 (component and/or breadboard validation in relevant environment) and in some applications even at 9 (successful operation in real-world application) such as the inclusion of liquid inside tires [6] or scratch-resistant automotive clear coats [7].

Frei et al. [5] define self-healing as a bottom-up approach, where the components of the system heal the damage from inside. These smart materials have the ability to repair small damages such as surface microcracks or fine scratches. The inspiration comes from biological systems which have the ability to heal themselves (bone regeneration, blood clotting, regrowth of deer antlers and so on) [8–10]. Typically, a damaged component is rehabilitated, but complete restoring to the original surface (stage) cannot be achieved with so far known healing methods.

The review by van Benthem et al. [11] clearly shows scope and limitations of self-healing and discusses damage formation and damage recovery on different size scales (micro, meso, macro). Damage to a polymeric coating material often occurs due to material fatigue, erosion, abrasion or UV exposure, or due to microcracks, which are formed underneath the surface of the coating material and therefore it cannot be noticed visually [12,13]. Once these cracks are formed they propagate until the coating material weakens and breaks, resulting in undesired modifications of material properties and decrease in performance. Superficial scratches (damage on a micro-level, degrading the decorative function) lead to microcracks (damage on a meso level, disabling the protective function) and finally to delamination (damage on a macro-level, destruction of the whole composite) [11]. In order to prevent these damages, new self-healing coating materials are being developed, which are able to respond to a damaging event and mend themselves, thereby significantly extending product durability.

Damage recovery always involves material flexibility within the organic polymer coating, individual motion of small molecules or visco-elastic flow of the polymer binder (Fig. 1) [11]. This material transport limits all self-healing approaches to the micro and meso scale.

Thermoplastics and thermosets can be designed as self-healing or have at least the potential to be healed. For instance, elimination of the effects of a damaging event, e.g., a scratch from thermoplastic materials (low glass transition temperature) occurs after a visco-elastic material reflow driven by forces due to surface tension and elastic energy imposed by the stress source. The surface texture levels out upon a temperature increase above the T_g and the material integrity is restored (Fig. 2). This type of healing involves molecular interdiffusion, surface randomization, recombination of chain ends, and similar processes. Therefore, the self-healing of thermoplastics is relatively simple [14]. Most of the recent studies on self-healing are focused on thermosetting polymers, because they are used in coatings, structural, lightweight and high end price applications. Thermosets are crosslinked via primary (covalent) bonds or sometimes via strong secondary hydrogen bonds [15]. These crosslinks prevent molecular motion of the polymer chains and thereby make intrinsic self-healing mechanisms (see Section 2.2) very difficult. A crack is formed when mechanical stress exceeds the elastic deformation of a thermosetting material. The energy is stored in the deformation of the surface and levelling through viscous reflow is not possible. The scratch remains as a permanent damage in the surface. Which means higher a materials T_g is, the higher is the scratch resistance. An ideal surface would have a T_g, that is sufficiently high to allow good resistance against minor scratches by elastic

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