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The microstructure of capsule containing self-healing materials: A micro-computed tomography study

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ABSTRACT

Autonomic self-healing materials are materials with built-in (micro-) capsules or vessels, which upon fracturing release healing agents in order to recover the material's physical and mechanical properties. In order to better understand and engineer these materials, a thorough characterization of the material's microstructural behavior is essential and often overlooked. In this context, micro-computed tomography (μCT) can be used to investigate the three dimensional distribution and (de)bonding of (micro-) capsules in their native state in a polymer system with self-healing properties. Furthermore, in-situ μCT experiments in a self-healing polymer and a self-healing concrete system can elucidate the breakage and leakage behavior of (micro-) capsules at the micrometer scale. While challenges related to image resolution and contrast complicate the characterization in specific cases, non-destructive 3D imaging with μCT is shown to contribute to the understanding of the link between the microstructure and the self-healing behavior of these complex materials.

1. Introduction

1.1. Self-healing materials

Today, one of the main incentives in material engineering is damage prevention. This leads to the reinforcing and often overdesigning of the engineered materials in order to prolong their life span without damage. As a consequence, engineered materials are often overused, while the final product still requires regular inspection and maintenance [1]. A solution for these problems is found in the development of materials with a built-in repair mechanism, or so-called self-healing materials. These materials have the potential of being more reliable, since they are capable of repairing (in)visible, internal and/or external damage. This results in a longer lifetime of the material [2]. Self-healing materials have been a topic of intense research for over 15 years [3–5]. During that time, different types of self-healing approaches were developed and tested for their healing efficiency in different material classes. The approaches can be divided in two main categories: autonomic self-healing, in which the healing agents are found in carriers added to the material, and autogenic self-healing, for which the material exhibits self-healing properties due to its composition [1,6–8]. Autonomic self-healing can be further classified based on the morphology of the healing agent's carrier. A first option is the sequestration of the self-healing agent in microcapsules, typically with a size ranging from 5 μm (e.g. in coatings) to 150 μm (e.g. in composites). Upon failure of the material, (micro-) capsules, are ruptured, releasing the self-healing agents into the region of damage. There, the healing agent reacts upon contact with moisture, air, or due to heating. In other self-healing systems, the healing agent needs to react with a catalyst which is encapsulated in an additional type of capsules and only provided to the fracture upon simultaneous rupture of both capsule types [7]. In the latter case, it is of course crucial for both components to be present in the area of damage in high enough quantities, so that the chemical reaction can take place [9]. A second autonomic self-healing approach is the vascular based system in which the healing agent is found in a network of hollow tubes or capillaries connecting the interior of the material with the exterior part. At the moment of primary damage, the healing agents flow out of the damaged capillaries, after which the network may be refilled by an external source, allowing for multiple local healing events [6,7].

Despite the significant efforts put into developing autonomic self-healing materials, relatively little attention has been directed to the

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characterization of the spatial distribution of the healing agent's carrier in the material matrix. Yet, this can severely influence the material's self-healing efficiency. Furthermore, better characterization of samples prior to, during and after mechanical testing can offer more insight into the efficiency of the applied technology, notably into the mechanical behavior of the carrier and the fluid mechanics of the self-healing agents released from these carriers. Most frequently however, the self-healing mechanism is only assessed by mechanical testing of the system, or through two dimensional (2D) analysis based on optical microscopy and scanning electron microscopy (SEM) [6,7]. This does offer the possibility to visualize fracture planes within different tested materials [10–13], however, carriers with healing agents can rupture subsequent to initial healing, during sample preparation for the 2D analysis.

High-resolution X-ray computed tomography (μCT) is a non-destructive 3D technique, which allows the study of carrier systems without having to disturb their state by cutting the material or opening a fracture. Based on a set of two dimensional (2D) radiographs taken from different angles, the sample under investigation is digitally reconstructed in three dimensions (3D) [14]. This allows the investigation of the internal structures and processes in a broad range of materials. Due to the rapid evolution of this technique over the last few years, it has become a widely available tool in the field of material science [15,16].

Despite the clear advantages of investigating autonomic self-healing systems with μCT, this technique has only recently started to gain importance in the field of self-healing [17–24]. μCT systems are now at the point that they allow the investigation of self-healing systems, almost regardless of the composition of the matrix material and self-healing agents. In this work, 2D and 3D analysis techniques are combined in order to characterize distribution patterns of carrier systems in different autonomic self-healing materials, as well as the leakage of healing agents from these carriers after failure of the material. The emphasis is put on the experimental procedure and the ability to adjust the set-up of experiments according to the visualization needs. The applied characterization workflows are invaluable to help predicting and explaining the efficiency of new self-healing material technologies.

2. Materials & methods

2.1. Materials

Two different self-healing materials, based on the autonomic approach, are analyzed: a polymer-based epoxy material, with self-healing properties due to the inclusion of microcapsules, and concrete, with self-healing properties obtained by embedded tubular capsules. For both cases, it is important to understand the distribution of healing agents in the material as well as the release of these agents upon failure.

Table 1
Overview of the conducted experiments.

Polymer-based epoxy + TetraThiol (and HDI_3) healing agent(s) in spherical microcapsules	Distribution of microcapsules within the matrix
	• Dispersion in the epoxy • Bonding of individual microcapsules
	Enhanced visualization of different types of capsules
	• Adaptation of epoxy matrix to a partially brominated epoxy
	Visualization of leakage from microcapsules in a newly formed crack
Concrete matrix + MEYCO healing agents in tubular capsules	Healing agent leakage in an ideal, predetermined crack

Table 1 provides an overview of the conducted experiments and their aim.

2.1.1. Self-healing polymers

2.1.1.1. Epoxy matrix. The commercial epoxy based on EPON 828 resin and DETA hardener has been used to build the self-healing materials. The synthesis and mechanical properties of these epoxy are well known and it is usually used as reference in self-healing [25].

2.1.1.2. Healing agents: Thiol-isocyanate capsules. A fast healing system was developed by Hillewaere et al. (2014), in which the healing agents are a tetrafunctional thiol-methyl benzoate mixture (TetraThiol) and multifunctional hexamethylene di-isocyanate isocyanurate trimer (HDI_3) in a 1:1 ratio (Fig. 1). Reaction of these chemicals results in the formation of strong polythiourethane-based networks, causing self-healing of the epoxy matrix. This system was developed to tackle some disadvantages of previously developed systems: the healing agents used in this system are low in toxicity, thermally stable and inexpensive [26]. At the same time, the reaction is efficient in the presence of moisture and air.

Microcapsules with solid melamine-formaldehyde walls, containing liquid TetraThiol in the core were prepared following the procedure reported by Yuan et al. (2008), while the microcapsules with HDI_3 as a liquid in the core, and solid polyuria were made by interfacial polymerization [27]. A detailed description of the synthesis of these microcapsules is found in Hillewaere et al. (2014). Through laser diffraction, using a Beckman Coulter LS 200 instrument, the authors determined the size distributions of both capsule types after they were sieved over a 500 μm mesh. This size distribution was also confirmed through scanning electron microscopy (SEM). Both capsule types had a mean diameter of around 150 μm. The choice of the TetraThiol – HDI_3 system within the EPON 828 epoxy yielded the most promising results for self-healing when compared to the virgin material [28]. However, it should still be noted that the inclusion of microcapsules can affect the mechanical properties of the initial polymer matrix: according to Brown et al. [25], it tends to strengthen the epoxy material through increased hackle markings and sub-surface micro-cracking. This, together with a reduction of the tensile strength and the Young modulus of the virgin samples, was also observed for the system under investigation here; for a full discussion, we refer to Hillewaere et al. [1].

2.1.1.3. Chemical adaptation of epoxy matrix for enhanced visualization. To investigate the 3D microcapsule distribution in an epoxy matrix, a mixture of the TetraThiol- and HDI_3 microcapsules was dispersed into EPON 828 epoxy resin and DETA hardener prior to curing of the epoxy resin. To remove any air after the homogeneous mixing of all components, a high vacuum was applied for 5 min. Then the solution could be poured in silicon molds, after which the epoxy with the embedded microcapsules was left to cure for 1 day at 25 °C and 1 day at 40 °C. The combination of the EPON 828 epoxy and DETA hardener was chosen because of the known catalytic effect of the epoxy matrix on the thiol-isocyanate reaction and promising healing efficiencies obtained in a previous study [26]. The Tapered Double Cantilever Beam (TDCB) test, with the protocol proposed by Brown et al. (2002) [29], was performed prior to X-ray CT scanning to test the (mechanical) healing efficiency of the system. In this quasi-static test, a crack is induced in the material by pulling apart both sides of the TDCB sample. The microcapsules were only added to the EPON 828 material around the symmetric plane along which the crack propagation is expected. In order to avoid a deviation of the crack out of the symmetric plane, TDCB samples with an initial groove along this plane were used (Fig. 2). The TDCB samples were subsequently pre-cracked using a fresh razor blade following the ASTM D4045 standard. After this, the epoxy material with the embedded microcapsules was loaded until the crack reached a visible length, avoiding