Assessment of self-healing capabilities, a route towards standardization

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ABSTRACT

In the last decade, an increasing attention has been given to the development of repairing capabilities in materials, with an emphasis in specific strategies that can promote self-healing, with or without external triggers. Self-healing has opened several new possibilities, especially in applications where long-term reliability is demanded and either maintenance or replace of these materials is difficult to perform.

Depending on the material class, different approaches in order to achieve self-healing, can be adopted. This led to distinct evaluation methods of the self-healing efficiency, depending on the material and its final use. One of the new challenges in self-repairing materials lays in the establishment of a common testing procedure for different materials classes, such as ceramics, concrete, polymers and composites. Normalized procedures can conduct to a standardization of the healing evaluation, which will set a common ground towards a better understanding of the concept and its quantification.

The assessment of self-healing capabilities is one of the major goals in the SHeMat project. SHeMat is a Training Network for Self-Healing Materials funded within the scope of the Seventh Framework Programme by the European Commission's Marie Curie programme. The focus of this work will be the development of a standard procedure and its applicability to the specific materials developed within the project. The comparative analysis of the results will act as a support to establish a common base for the definition of self-healing as a quantifiable characteristic. This discussion covers the work that has been conducted so far in the SHeMat project and possible future directions.

1. INTRODUCTION

The assessment of self-healing capabilities in materials depends not only of the specific type of material but also on the healing process by itself. Self-healing process can be divided into three different types depending on how the capability is developed: by physical or chemical interactions working autonomously or triggered by external stimulation. The strategy adopted to evaluate the self-healing capabilities must therefore consider the way that this property is developed. Healing can refer to a wide range of properties and can be evaluated considering the tensile strength, strength recovery or the fracture behaviour, among others. This assessment also depends on the repairing mechanism: if it is based on a microencapsulated healing agent, an additive or if it is caused by an external stimulus (temperature, electrical or magnetic field) [1].

2. ASSESSMENT OF SELF-HEALING IN MATERIALS

2.1. MACROSCOPIC APPROACH

Several authors try to develop and adopt a standard quantification formula to assess self-healing capabilities, with the goal of setting a common ground that allow comparisons between different works. The evaluation of the stress–strain response under both quasi-static and high loading rate deformation conditions in polymers is fundamental to understand the deformation history of the material over the initial loading cycles. For quasi-static fracture conditions, healing efficiency is defined in terms of the recovery of fracture toughness. Healing evaluation starts with a virgin fracture test of an undamaged tapered double cantilever beam (TDCB, Figure 1). Prior to testing, a pre-crack was created with a fresh razor blade into the centre groove of the specimen. The damage is introduced to sharpen the crack-tip, while loading increased until the crack propagates along the centreline of the sample until failure. The crack is then closed and allowed to heal at room temperature (without any external intervention). After healing, the sample is loaded again until failure [2].

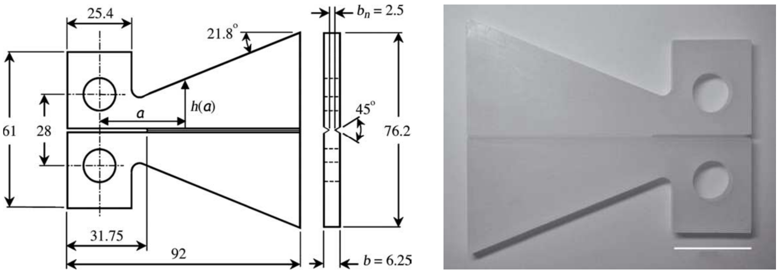

Figure 1 – example of a TDCB sample.

Static fracture tests evaluate the changes in the crack growth and the absolute fatigue life of the healed material [3]. The fatigue response of the self-healing material is dependent of a wide number of factors, such as stress intensity, healing periods, among others. With this assessment method, it is possible to evaluate the recovery after the induced damage caused by cyclic loading [4]. The healing efficiency λ, can be determined by the correlation between the fatigue life-extension (Equation 1).

$$\lambda = \frac{N_{healed} - N_{control}}{N_{control}} \qquad \text{Equation 1}$$

Where N_{healed} stands for the total number of cycles until the failure of the healed sample and $N_{control}$ the total number of cycles until the failure of a non-healed sample

For elastomeric self-healing material, the fracture toughness protocol with the TDCB-sample configuration may not be the most suitable model to evaluate the healing performance, since elastomers can fail through fracture and fatigue processes. [5]. Instead of evaluating the fracture toughness, it should be assessed the tear strength recovery. For this purpose, some authors developed a specific rectangular specimen (Figure 2).

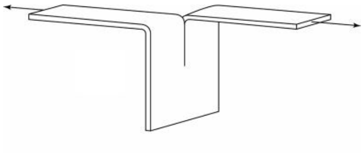

Figure 2 – example of a rectangular sample.

Healing efficiency η, can be defined as the recovery of the tear strength of the healed sample (T_{healed}) compared to the non-damaged one (T_{virgin}), according to Equation 2.

$$\eta = \frac{T_{healed}}{T_{virgin}} \qquad \text{Equation 2}$$

Depending on the material and the properties under evaluation, the technique and the self-healing quantification method change, becoming difficult to compare performances and establish standards.

The main challenge remained in the development of a suitable method to evaluate the healing efficiency. Until recently, the focus has been the macroscale evaluation of the healing properties, usually with a complete separation of the material during the tests. However, this is not enough to provide a comprehensive evaluation of what happen inside the material when the first microcracks start to develop. To achieve a quantitative evaluation for the relationship between the material structure and the self-healing properties of the system an extra emphasis on in situ microscopic measurements is essential.

2.2. MICRO AND NANOSCALE EVALUATION

One of the most important causes for material failure during service is the development of multiple microcracks. The propagation of these cracks lead to severe damage, the leading cause for loss of performance. Mechanical testing of materials with microindentation techniques has become widely accepted as a viable tool. It is even regulated recently, by international standards [6]. This technique can be easily applied to hard materials however, its application to softer materials need to be considered more carefully [7]. Instrument calibration, strain effects, and material heterogeneity are examples of possible complications that arise when small volumes of polymers are tested. However, with a proper setup planning it is possible to test these materials and obtain reliable data from this technique [8].

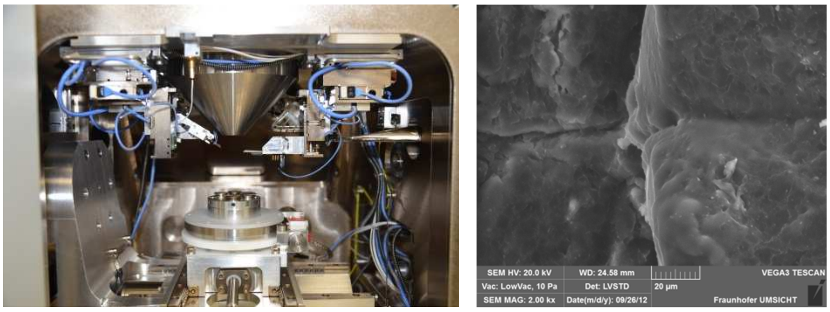

Figure 3 – Equipment for microcutting, inside the UMSICHT ESEM (left) image of a healed cut, elastomer sample (right)

These data, when complemented with the macroscopic bulk methods, retrieve important information regarding the micro and nanoscale self-healing of polymers. The analysis of the damaged surface morphology can provide essential information concerning the evolution of the healing reaction and crack propagation. This analysis can be performed with an environmental scanning electron microscope (ESEM) (Figure 3). The self-healing process can be studied by inducing mechanical damage through micromachining, followed by imaging of the repair process.

This can be an important tool to produce and analyse the damage in a material surface. This technique as evolved in recent years, can now be used to characterize several mechanical properties (elastic modulus, flexural strength, compression, etc.).

3. CONCLUSIONS

The macroscale evaluation by itself is not sufficient to establish standard parameters for the self-healing quantification in materials. Using microscopic evaluation techniques it will be possible to relate the behaviour of a single static defect to the self-healing ability, rather than an evaluation by a collective behaviour of defects. One obstacle that has delayed the implementation of the microscopic self-healing evaluation concerns to the very small volume of the samples. Considering the nonhomogeneous composition of some materials, sampling can be challenging. The preliminary tests, conducted at Fraunhofer UMSICHT proved the viability of this technique, however further improvements need to be done, so that it can be accepted as a standard method.

Microindentation technique can be used in several different classes of materials to measure numerous materials properties. This can be a useful step towards the standardization of the self-healing quantification process. Establishing a standard is one key step for the industrialization of self-healing materials.

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