CRACK PROPAGATION IN MICRO-ENCAPSULATED POLYMER FOR SELF-HEALING: NUMERICAL MODELLING AND EXPERIMENTAL VALIDATION

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Abstract
Self-healing materials are currently in several areas of research, from polymers to cementitious materials. These smart materials have the ability to repair damage caused by mechanical usage, such as cracks, avoiding or delaying the mechanical failure. Although self-healing materials are very attractive for several applications, it is important to know pros and cons. We have numerically studied the crack propagation in homogenous and micro-encapsulated polymers in order to model the behaviour of the self-healing polymers. The results will be used to design and optimize micro-encapsulated polymers for self-healing.

1. Introduction

Polymer composites are demanded by engineering industries because of their advantages which are light weight, chemical stability and good manufacturing among others. Some examples of high performance products are aircraft components, bicycle frames, racing car bodies and also orthopaedic surgery. These industries demand new composites with excellent mechanical properties and high reliability. Self-healing materials add the ability of autonomous repair increasing the reliability and lifetime [1]. The first approach to self-healing composites starts with the study of self-healing polymers.

Although there are several self-healing concepts [2], this study focuses on micro-encapsulated polymers. These polymers have dispersed microcapsules with healing agent and a catalyst chemical trigger inside the matrix [3,4]. The healing begins when a propagating crack ruptures the microcapsules. Then the released healing agent is drawn into the crack plane where it is polymerized in contact with the catalyst. Therefore, the structural integrity across the crack plane is re-established.

It is noteworthy that the microstructure of the self-healing polymer with embedded microcapsules modifies the properties of the homogeneous material. For example, the ultimate strength and the elastic modulus decrease in polymers which have micro-capsules for self-healing [5]. The deterioration of some properties can be a disadvantage and can limit the

use of self-healing polymers in some applications. Pros and cons are discussed in this paper for some applications.

Once decided to use self-healing polymers, they must be characterized. The quantification of the healing efficiency was defined as the ratio of healing to virgin fracture toughness [3]. Several studies of self-healing polymers [4–6] have used the same experimental set-up to measure and optimize the different configuration and compounds of self-healing polymers. The Tapered Double-Cantilever Beam (TDCB) specimen is used for measuring the healing efficiency. In this work we highlight the details of the TDCB geometry and the experimental set-up which are modelled later.

Numerical simulations of crack propagation have been performed to study the behaviour of self-healing polymers. First, simulations based on the eXtended Finite Element Method (XFEM) have been used to model TDCB specimen. Finally, simulations of small scale models are used to design and optimize micro-encapsulated polymers for self-healing.

2. Advantages and disadvantages of self-healing polymers

Before using a self-healing polymer in a specific application, one must study the advantage and disadvantages of the material. In this section, some limitations in the use of self-healing polymers are discussed.

The main advantage of self-healing polymers is the ability to repair the structural damage produced by crack propagation. But the introduction of microcapsules into the matrix changes the microstructure. Indeed, one can consider the microcapsules as defects in the polymer. Table 1 shows some pros and cons of using self-healing polymers. The change in the microstructure of the polymer can induce a deterioration of some mechanical properties, although other properties can be improved. In a self-healing polymer the concept of damage prevention is substituted by the concept of damage management [1]. Therefore, the development of new strong materials to prevent mechanical failure is changed for the development of smart materials to control the progression of the mechanical failure. Other disadvantage can be a complex production of the final product or the increment of the costs. Finally, one can consider self-healing polymers as a source of new application. Sometimes the wheel is invented before the car.

Pros	**Cons**
Ability to repair	Introduction of defects
Increase some mechanical properties	Decrease some mechanical properties
Damage management	Damage prevention
	Complex production
New applications	Elevated costs

Table 1. Pros and cons of self-healing polymers.

It is easier to discuss the pros and cons in a particular case. We have selected the self-healing polymer with microcapsules used by Brown et al. [5–7]. The matrix is EPON epoxy resin and DETA curing agent with a concentration of 17% in volume of microcapsules. The healing agent, Dicyclopentadiene (DCPD), was encapsulated in urea-formaldehyde microcapsules of 180 microns of diameter. Mechanical properties of neat epoxy EPON are compared with the self-healing polymer in table 2. These properties have been obtained without any action of the self-healing agent. The Young's modulus and ultimate stress decrease when microcapsules

are introduced into the matrix. One can consider that the material has voids (defects) of the same size of the microcapsules, so the stiffness of the polymer decreases. That reduction of mechanical properties can limit the application where this self-healing polymer can be used. On the other hand, the fracture toughness is higher in the self-healing polymer. The reason is that the microcapsules make more difficult the crack propagation, acting as stoppers and diverting the crack path. In addition, the self-healing process ensures the recovery of the fracture toughness after crack initialization when the healing agent has been cured. The time of curing is another factor to take into account. Fast curing healing agents can be useful for polymers that must withstand fast cyclic loading or impacts. It is reported that the DCPD healing agent gets its maximum healing efficiency after 10 hours.

Property	Neat epoxy	Self-healing
Young´s modulus (GPa)	3.4	2.8
Ultimate stress (MPa)	39	20
Fracture toughness (MPa m1/2)	0.55	1.25
Healing efficiency (%)	-	55
Curing time (hours)	-	10

Table 2. Mechanical properties of neat epoxy (EPON) and self-healing polymer (EPON with embedded microcapsules) [4,5]

The proposed self-healing polymer will be a good option for a wind turbine blade where low cyclic loading is expected. In this scenario, the retention of the crack propagation due to the higher fracture toughness and the self-healing process enhances the lifetime of the blade. Other points to consider are the self-healing polymer production and costs. The production can be easily implemented because microcapsules can be added when resin and curing agent are mixed. The estimation of the micro-encapsulation cost for an industrial application is, however, more difficult.

As a conclusion, whether pros outweigh cons depends on the specific application. It is necessary to characterize the self-healing polymer, mechanical properties and self-healing process, to have a global view.

3. Self-healing efficiency

The studies about self-healing polymers quantify the self-repair from the final properties of the healing material and the initial properties of the virgin material [8]. The most common value to quantify the self-healing ability is the ratio between the healed and virgin fracture toughness. Therefore, healing efficiency is defined as $\eta = K_{IC}^{healed} / K_{IC}^{virgin}$ [3,4]. Several works use the TDCB geometry to simplify the measurement of the fracture toughness [4,5,9,10]. With this geometry, the fracture toughness is independent of the crack length and only depends on the applied force, $K_{IC} = \alpha \cdot P_C$, where α is a function of the geometry and the material properties, and P_C is critical load at fracture. As a result, healing efficiency is the ratio of the critical loads, $\eta = P_C^{healed} / P_C^{virgin}$.

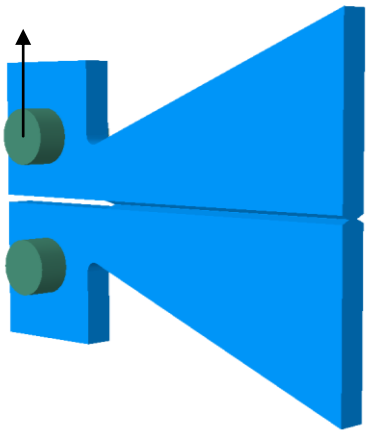

Figure 1. Representation of TDCB set-up in 3D. The TDCB specimen (blue) is supported by two pins (green).

Figure 1 shows the set-up of the experiment with the TDCB specimen. The specimen is supported by two pins which allow free rotation along their axis. During the experiment, a constant vertical displacement is applied in the upper pin while the lower pin is fixed. The reaction force in the upper pin is represented as a function of the displacement of the same pin (see figure 2).

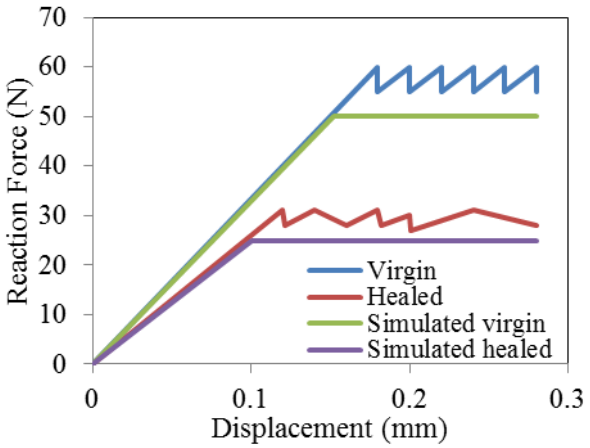

Figure 2. Representative curves, reaction force (N) versus displacement (mm) of the upper pin during the experiment with TDCB.

Healing efficiency is assessed using the protocol established by White et al. [3]. The experiment with the TDCB is performed two times. First, the virgin specimen is loaded until a crack is propagated along the sample but without breaking the specimen completely. When the reaction force reaches the critical load P_C, the crack propagates unstably a certain length and the load falls suddenly (see virgin curve in figure 2). Then the reaction force increases again while the displacement continues until the reaction force reaches again P_C. The stick-slip behaviour is usual for the TDCB geometry [11,12]. Then, the TDCB is released from the pins and is allowed to cure itself. After the curing, the specimen is loaded again, increasing the displacement of the upper pin until the crack propagation. The healed curve represented in figure 2 shows a different behaviour than the virgin one. The slope can be different and the critical load of the healed curve is usually lower. Moreover, the healed specimen shows less uniform stick-slip behaviour during crack propagation. Dividing the healed critical loads by the virgin one, one obtains the healing efficiency. Brown et al. [5] reported a healing efficiency of 55% in this self-healing polymer.

Although Young's modulus and ultimate strength of the self-healing polymer are not necessary to obtain the healing efficiency, they are usually calculated with the ASTM standard 638 [4]. In addition, the fracture toughness can be computed with more or less accuracy from TDCB experiments [10].

4. Simulation of self-healing polymers

We have studied self-healing polymers via simulations in order to understand the crack propagation and healing behaviour. Finite element simulations have been performed with ABAQUS commercial software. Two kinds of simulations have been carried out: simulation of the TDCB and numerical homogenization.

4.1. Simulation of the TDCB

Although the experimental set-up of TDCB for self-healing polymers has been used in several studies, there are few numerical simulations that address this set-up and its characteristics [13].

In TDCB simulations we have assumed that the polymer is homogeneous with uniform properties, because we are interested in the simulation of crack propagation. Mechanical properties from experiments have been used in these simulations. The microstructure of the self-healing polymer is studied in the next section.

Geometry and boundary conditions have been defined as the actual experiment (see figure 1). The solution is calculated under the assumption of quasi-static simulation, so the velocity of the pin displacement is irrelevant. We have used the cohesive damage model based on eXtended Finite Element Method (XFEM) to simulate the crack propagation. Results show that the reaction force increases with the displacement of the upper pin until reaching a critical load. Then, the reaction force remains constant while the crack propagates along the path (see simulated virgin curve in figure 2). There is no stick-slip behaviour in the numerical solution. The critical load and displacement can be validated with the experimental data of the virgin specimen.

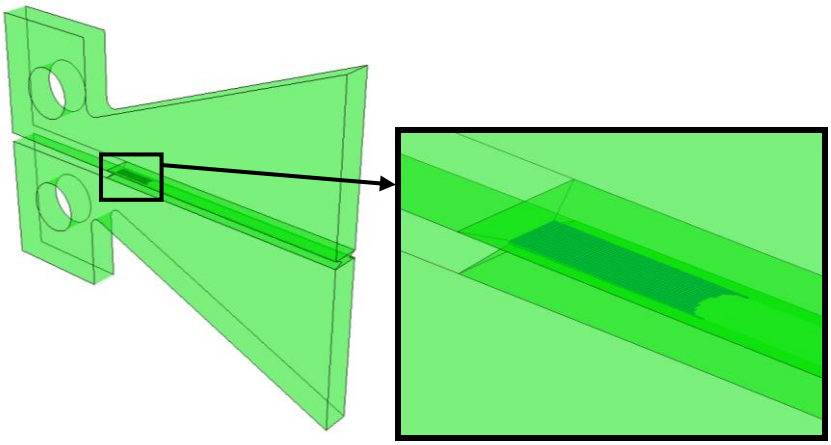

Figure 3. Detail of crack profile during crack propagation in TDCB geometry.

The profile of the crack tip is curved, advancing faster at the edges of the beam due to the two grooves along the crack plane that guide the crack propagation (see figure 3). We have

performed a boundary condition and mesh sensitivity analysis of the numerical model. Simulations show that any small asymmetries to the crack plane must be avoided because they induce a deviation of the crack propagation. This sensitivity can be the reason why the experiment is difficult to reproduce and the results have a high dispersion.

Healed specimen can be also simulated (see simulated healed curve in figure 2). For this simulation the crack plane is modelled using the Cohesive Surface (CS) method, where maximum tension stress and fracture energy are defined for this surface independently from the polymer properties. The critical load depends of the properties of the CS that represent the healing agent after the curing.

Extra information can be obtained from the simulations of crack propagation. For example, the evolution of the strain field at the side surface of the beam during the crack growth can be compared with the experimental data from Digital Image Correlation (DIC) technique.

4.2. Numerical homogenization

We carried out simulations in a small scale domain where capsules around two hundred microns diameter are dispersed within the bulk polymer. The final objective is to simulate the microstructure of the self-healing polymer and obtain the global properties.

There are studies of homogenization of different microstructures using damage models where crack propagation is not considered [14,15]. We have introduced the simulation of crack propagation along the microstructure where there are two different materials, bulk polymer and the shell of microcapsules. The microcapsule distribution, the interaction microcapsule-polymer and microcapsule thickness have also been taken into account.

In these simulations, the use of XFEM for crack propagation is combined with CS to describe the interaction of the capsule-matrix interface. General properties can be estimated from the representative volume element (RVE), as it is shown in figure 4. From these results, we can obtaine the behaviour of crack propagation and the properties of the self-healing polymer for different microcapsule size, volume fraction and microcapsule thickness.

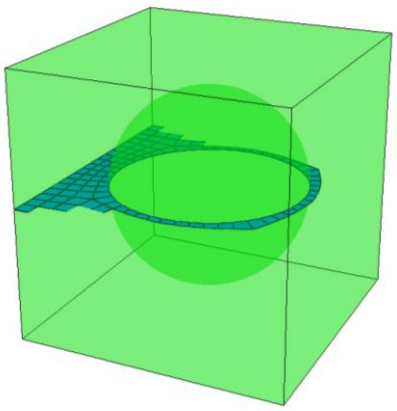

Figure 4. RVE of the self-healing polymer with microcapsules of 180 microns diameter. Crack propagation along the middle plane of the volume.

The objective of these simulations is the optimization of the design parameters such as radius and thickness of the microcapsules and volume fraction. Finally, the information from these

simulations is expected to provide valuable feedback to complement the experiments and simulation of the TDCB.

5. Conclusions

Advantages and disadvantages of self-healing polymers have been discussed. Pros and cons are subjected to the final application. Therefore, a good characterization of the self-healing polymer and a detailed study of production and costs is required.

Healing efficiency of self-healing polymers can be obtained from TDCB specimens, but numerical simulations are needed to understand the behaviour of the experiment and prevent mistakes.

Two different simulations have been carried out, the first focuses on crack propagation in TDCB geometry and the second on small scale domain with self-healing polymer microstructure. Simulations of the TDCB give results that can be compared with experimental values, adding extra information. Moreover, the simulations of the microstructure can optimize the size and volume fraction of the micro-encapsulated self-healing polymers.

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