Materials and Design 116 (2017) 538–544

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Nano-reinforced polymeric healing agents for vascular self-repairing composites

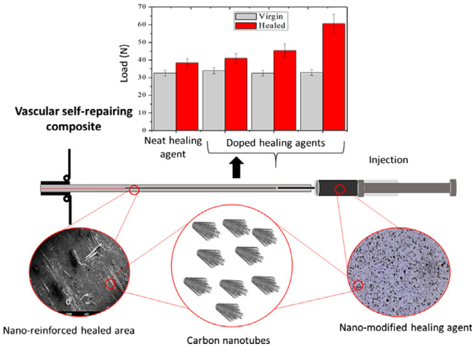
D.G. Bekas, D. Baltzis, A.S. Paipetis *

Materials Science & Engineering Department, University of Ioannina, Ioannina 45110, Greece

HIGHLIGHTS

- The nano-modification of a healing agent for vascular self-repairing fiber reinforced composites via CNTs was studied
- The dynamic viscosity of the healing agents was assessed at different filler loadings
- Healing efficiency of the system was evaluated in terms of interlaminar fracture toughness
- The nanoreinforcement of the healing agent resulted in significant fracture toughness and healing efficiency improvements
- Scanning Electron Microscopy revealed additional energy consumption mechanisms for the reinforced healing agents

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 October 2016
Received in revised form 17 December 2016
Accepted 18 December 2016
Available online 20 December 2016

Keywords:
Self healing composites
Nanoreinforced healing agents
Carbon nanotubes
Vascular network
Double cantilever beam tests

ABSTRACT

In this study, the nano-reinforcement of an epoxy healing agent for vascular self-repairing fiber reinforced composites, is explored for the first time. Multi Wall Carbon Nanotubes (MWCNTs) have been selected, as the nanoscaled reinforcing phase of a low-viscosity epoxy healing agent, in three different weight contents. The rheological behavior of the nanomodified epoxies was evaluated via apparent dynamic viscosity measurements and adjusted accordingly. The resulted nanocomposites were infused via a vascular network, to Double Cantilever Beam (DCB) fractured Glass Fiber Reinforced Composites (GFRPs) specimens in order to assess the effect of the MWCNTs on the healing efficiency (η), in terms of maximum bearing load and interlaminar fracture toughness (G_{Ic}) recovery. The employment of the nanoenhanced healing agent increased the calculated healing efficiency (n_{GIc}) up to circa 190%, through the introduction of additional energy consumption mechanisms that were confirmed via a comparative Scanning Electron Microscopy (SEM) study.

1. Introduction

Due to their excellent mass-specific mechanical properties as well as their “tailor-to-order” strength and stiffness, fiber reinforced polymer (FRP) composites are widely used in several industrial sectors such as the automotive, aerospace, naval and renewable energy. There is, however, an important drawback when FRPs are subjected to mechanical loading which concerns the susceptibility of these materials to microcracking or delamination that may be created deep within the microstructure, due to their poor through-thickness strength and toughness. As is well known, the detection of these defects from the surface of

---

* Corresponding author.
E-mail address: paipetis@cc.uoi.gr (A.S. Paipetis).

http://dx.doi.org/10.1016/j.matdes.2016.12.049
0264-1275/

the composite is a strong challenge for non-destructive evaluation (NDE) techniques and the subsequent repair, in most of the cases, is very difficult and costly to apply [1–4].

Apart from conventional damage tolerant design philosophies, the self-healing concept has attracted great interest in the research community over the last decade [5–7]. Inspired by living organisms, self-healing composites possess the remarkable ability to detect and heal damage and, as a result, to restore their initial performance (fully or partially). Self-healing composites can be categorized into three conceptual approaches, the intrinsic, the vascular and the capsule-based. The intrinsic self-healing approach exploits the inherent ability of a composite to restore its initial properties, at the molecular level, through physical or chemical reversible bonding, theoretically for an infinite number of repetitions [8–12]. The capsule-based concept is an extrinsic self-healing mechanism that involves the embedment of capsules, which contain an active liquid i.e. the healing agent, within the host material. When the composite is damaged, the capsules are ruptured, releasing the liquid agent at the damage site thus repairing the material [13–15]. An alternative route towards developing self-repairing composites is by mimicking the blood vessels of living organisms. This approach, involves the fabrication of a vascular network composed of micro-channels or hollow fibers whereby the healing agent is manually or automatically introduced into the host matrix [16,17]. Upon damage of the vascular network in the presence of crack propagation phenomena, healing is performed as the healing agent is delivered to the damaged area. In the case where the healing agent is injected in the vascules via an external intervention, this approach deviates from a per se self-healing process. However, it is widely accepted in the research community as a self-healing technology [18,19].

The bio-mimetic vascular self-healing FRPs, have been extensively studied due to the variety of healing agents that can be employed and the large scale of damage that can be healed, spanning from matrix cracks to large scale delamination [20]. In a representative study by Norris et al. [21], a vascular network was fabricated which combined damage sensing and healing capabilities within an advanced FRP composite. When these vascules were ruptured, due to a low-velocity impact event, the damage was detected using pressure sensors triggering the delivery of a low-viscosity epoxy healing agent from an external reservoir, to the damage site. In a more recent study, Coope et al. [22] presented a vascular self-healing FRP composite, capable of recovering its initial fracture toughness after Mode I crack opening displacement, by employing a Lewis acid-catalyzed epoxy self-healing agent. The viscosity of the epoxy was adjusted using ethyl phenylacetate (EPA) solvent, while the vascular network was created parallel to the fiber direction using poly(tetrafluoroethylene) (PTFE)-coated steel wires.

It is evident that one of the most critical aspects that affect the development of a smart and efficient vascular self-repairing composite structure is the selection of a proper healing agent. The delivery mechanism, as well as the physical and chemical properties (i.e. viscosity, curing time etc.) of the healing agents, are fundamental to the repairing process as well as to the restoration of the mechanical properties of the composite.

An unwanted side effect of the healing process in vascular FRPs is that the damaged area (i.e. delamination) inevitably becomes a resin rich region which may act as a crack initiation site due to the absence of primary fiber reinforcement. A reliable route towards eliminating this effect, may be that of the nano-reinforcement of the infused healing agent through the incorporation of nanoscaled fillers such as carbon nanotubes (CNTs) [23]. Possessing exceptional mechanical properties, low mass density and high surface-to-volume ratio, CNTs have been proved as excellent candidates for reinforcing epoxy resins and hybrid FRP composites [24–29]. However, the addition of CNTs within an epoxy resin leads to a significant viscosity increase of the polymer system due to their high surface-to-volume ratio [30–32], a property that plays a decisive role to the effectiveness of a vascular self-healing system.

Summarizing, the scope of this work is the nano-reinforcement of a low viscosity epoxy resin via the incorporation of multi wall CNTs (MWCNTs) and the employment of this nanocomposite as a healing agent in vascular glass fiber reinforced polymer composites (GFRPs). As the rheological behavior of the healing agent is a crucial parameter in the development of an efficient self-repairing system, the viscosity of the nanomodified healing agents, has been monitored and adjusted using EPA as a solvent. The vascularized GFRPs were subjected to quasi-static mode I interlaminar fracture toughness tests, using the double cantilever beam (DCB) coupon specimen geometry, so as to examine and evaluate the effect of MWCNTs to the interlaminar fracture toughness and consequently to the healing efficiency of the system [33]. A comparative scanning electron microscopy (SEM) study on the fractured surfaces of the healed specimens was also conducted in order to gain an insight on the morphology of the laminates fracture process.

2. Experimental

2.1. Materials

A two-part low viscosity epoxy resin system, i.e. the Araldite LY 5052 and Aradur 5052, supplied by Huntsman Advanced Materials, Switzerland at a mix ratio of 100:38 by weight, was used both as the GFRP matrix material as well as the healing agent. This epoxy resin-polyamines hardener system was selected due to its low viscosity and easy impregnation of reinforcement fabrics. As a healing agent, it was modified using MWCNTs supplied by ARKEMA, France with typical diameters and lengths ranging from 10 to 15 nm and 1 to 10 μm, respectively. MWCNTs were produced via Catalyzed chemical vapor deposition (CVD). Unidirectional GFRPs were manufactured using E-glass unidirectional fabric supplied by R&G, Germany while EPA solvent was purchased from Sigma–Aldrich.

2.2. Specimen preparation

Four laminates were manufactured for each healing agent scenario (i.e. neat, doped 0.1–0.3 and 0.5 + EPA), using 16-plies of unidirectional glass fabric with areal density 220 g/m^2 and lamina thickness of 0.242 mm. The hand lay-up method was selected as the manufacturing process, with a curing cycle at 25 °C for 24 h and applied pressure of 10^7Pa while post curing took place at 100 °C for 4 h under the same pressure. Spacers were used in order to achieve uniform laminate thickness of 3.9 mm. The vascular network within the composites was created using nylon strings (0.6 mm diameter), placed at the mid-plane of the laminate parallel to the fibers direction. An 18-μm-thick teflon release film (PTFE) was placed in the mid-thickness plane of the laminate to act as initial pre-crack according to ASTM-5528 [33]. At the end of the curing process, the nylon strings were manually pulled out and the GFRP plates were cut to DCB specimen geometry. A two-part epoxy adhesive namely Epocast 52 A/Epibond 1590 was used to glue pairs of piano hinge tabs at the end of each specimen as shown in Fig. 1. Prior

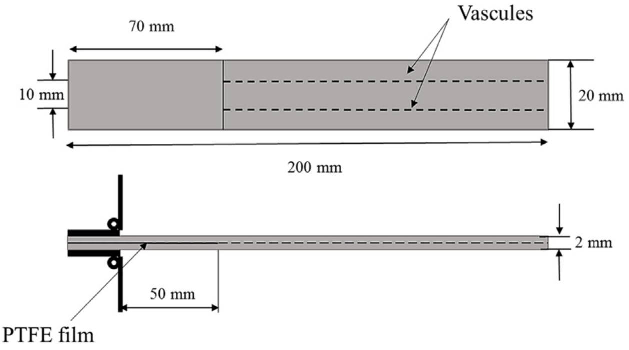


Fig. 1. Double Cantilever Beam (DCB) coupon specimen geometry.