Composites Part B 78 (2015) 515–519

Contents lists available at ScienceDirect

Composites Part B

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

Mechanical properties of a self-healing fibre reinforced epoxy composites

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ARTICLE INFO

Article history:
Received 1 December 2011
Received in revised form
8 April 2015
Accepted 12 April 2015
Available online 18 April 2015

Keywords:
A. polymer-matrix composites (PMCs)
B. Smart materials
C. micro-mechanics
D. Mechanical tests
Self-healing

ABSTRACT

Inspired by biological systems in which damage triggers an autonomic healing response, a polymer composite material that can heal itself when cracked has been developed. In this work, compression and tensile properties of a self-healed fibre reinforced epoxy composites were investigated. Micro-encapsulated epoxy and mercaptan healing agents were incorporated into a glass fibre reinforced epoxy matrix to produce a polymer composite capable of self-healing. The self-repair microcapsules in the epoxy resin would break as a result of microcrack expansion in the matrix, and letting out the strong repair agent to recover the mechanical strength with a relative healing efficiency of up to 140% which is a ratio of healed property value to initial property value or healing efficiency up to 119% if using the healed strength with the damaged strength.

1. Introduction

The durability and reliability of widely used polymer materials are often a concern due to mechanical loading and UV rays damage, etc. They experience microcracks that are developed as a result of damage. To overcome this, self-healing polymeric materials having a built-in capability are developed to substantially recover their load transferring ability after damage. This field of self-healing materials is beginning in the early 1990s, with the majority of the research occurring in the past decade [1–3].

In a materials engineering context, the concept of self-healing may be applicable where manufacturing or operationally induced damage can be repaired by materials already contained within the structure. In recent years, research groups [4] have developed discrete, bio-inspired concepts for autonomous delivery of a mobile fluid phase from either microcapsules or hollow fibres to effectively repair fibre-reinforced polymer composites. This concept has been furthered with the introduction of integrated, pervasive vascular networks at the micro- and meso-scale, demonstrating a replenishable and repeatable self-healed function [4].

A variety of encapsulated repair agents have been incorporated into self-healing materials. Urea Formaldehyde (UF) microcapsules containing the liquid monomer dicyclopentadiene (DCPD) have been utilized in the initial metathesis-based self-healing system [5,18]. Other microcapsule-based self-healing systems include chemistry based on polydimethylsiloxane, tungsten-catalyzed metathesis of bicyclic monomers, and activation of latent functional groups with common organic solvents and epoxy-solvent mixtures [5]. Autonomic self-healing occurs when damage in the matrix ruptures the microcapsules, releasing the contained monomer into the crack plane, which then polymerizes. Initial studies on the recovery of mechanical properties in self-healing materials have focused on monotonic fracture testing and fatigue. However in recent studies, Kessler et al. have demonstrated incorporation of the self-healing system into a woven fiber-reinforced composite and exhibit recovery in fracture toughness after Mode I failure [6].

Several other self-healing strategies in polymers have also been proposed. Chen et al. have developed a polymer that can repair cracks based on a thermally reversible Diels–Alder cross-linking reaction,

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http://dx.doi.org/10.1016/j.compositesb.2015.04.014
1359-8368/

allowing for re-mending upon heating [7]. Another solid-state system, demonstrated by Hayes and co-workers, utilizes a thermoplastic phase dissolved in an epoxy matrix [8]. Yin and co-workers have proposed a microencapsulated healing system with epoxy healing agent embedded in a woven fibreglass-reinforced epoxy composite containing latent imidazole curing agent [9] which heals at elevated temperatures (140 °C). Systems based on the delivery of liquid healing agent from embedded tubes have also been proposed and investigated by several authors. This idea was proposed by Dry [10]. The aforementioned healing systems are not autonomic; that is, they require some form of external intervention (temperature, heat, manual fluid injection, etc.) for healing and recovery.

Williams et al. [11] conducted the compression after impact (CAI) experiments at 3 J, demonstrating 95% retention of CAI strength compared to 66% for unhealed panels. Using the microencapsulated epoxy and latent curing agent approach, Yin and coworkers [9] measured CAI of woven fiberglass-reinforced epoxy composites impacted up to 3.5 J, showing improved healing performance at lower impact energies and through application of lateral pressure. Another study demonstrates fully autonomic self-healing of low-velocity impact damage in a fibre-reinforced composite. Self-healing functionality is integrated in a conventional woven glass-reinforced epoxy composite [6]. John et al. [12] reported a new sandwich, which is an orthogrid stiffened shape memory polymer (SMP) based syntactic foam core. The compression results demonstrated that the healing efficiency, a ratio of healed property value to initial property value, was over 100% for almost all the impact-healing cycles.

In this study, microencapsulated epoxy and mercaptan healing agents were synthesized and incorporated into a glass fibre reinforced epoxy matrix to produce a polymer composite, capable of self-healing. Compression, tensile and microstructure of epoxy composites were examined.

2. Materials and methods

Two types of epoxy resins were employed. One was diglycidyl ether of bisphenol A (Euroxsys Ltd.) acting as the matrix polymer, and the other was diglycidyl tetrahydro-o-phthalate (DTHP, Jindong Chemical Plant, Tianjin, China) with epoxide equivalence weight of 0.65 mol (100 g)−1 as the polymerizable component of the healing agent. Accordingly, two types of curing agents were used. They are diethylenetriamine (DETA) supplied by Shanghai Medical Group Reagent Co. (Shanghai, China) working for pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) with hydrosulfide group content of 26.55%, purchased from Fluka Chemie AG (Buchs, Switzerland). The catalyst benzyl dimethylamine (BDMA) with boiling point of 183.5 °C was purchased from Shanghai Medical Group Reagent Co. (Shanghai, China).

Epoxy prepolymer (400.0 g) was added to a 2 wt% aqueous solution of sodium styrene–maleate copolymer (1200 ml). The mixture was vigorously stirred for 5 min and then a few drops of 1-octanol were added to eliminate surface bubbles of the epoxy emulsion. The prepolymer of melamine (62.5 g) and 37% formaldehyde (135.5 g) was synthesized at 70 °C for 30 min and pH value of the solution was kept at about 9–10 by adding triethanolamine. Subsequently, the prepolymer solution was added to the above epoxy emulsion at 50 °C with continuous agitation for 1 h while pH value of the system was kept at about 3 by adding citric acid. Eventually, the reaction mixture was cooled down to room temperature and the deposit of microcapsules was separated through a Buchner funnel, rinsed with deionized water and vacuum dried. The microcapsules containing the hardener were prepared in two steps. Firstly, mercaptan was microencapsulated in a similar way as that adopted in making epoxy-loaded microcapsules. Then, the microcapsules were uniformly dispersed into catalyst solution (BDMP) at 40 °C for a certain time (0.5–24 h), filtrated, rinsed with ethyl ether and dried at room temperature [13,14].

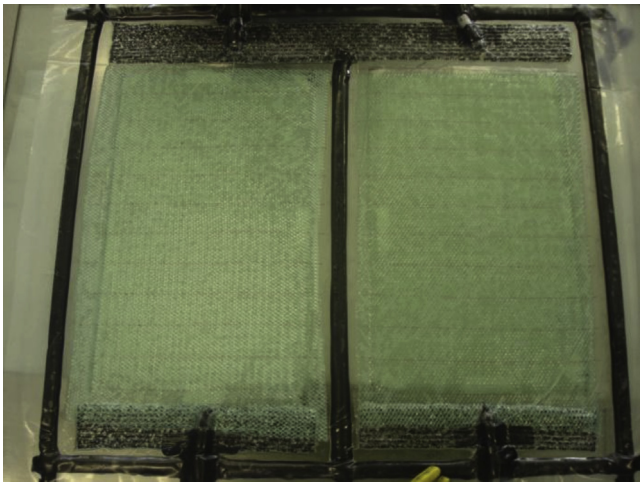

Fig. 1. Resin infusion set up.

The unfilled epoxy specimens were produced through mixing epoxy resin with hardener. The feeding amount of epoxy-loaded microcapsules should be equal to that of hardener-loaded microcapsules due to the requirement of stoichiometry of the mix. The total concentration of the microcapsules in the matrix epoxy is 2.5 and 5 wt %. The speed of agitation should be properly selected. Very high agitation speeds would lead to breakage of the capsules during mixing and very slow results in uneven distribution. Having it well mixed, the curing agent is added in the ratio of 100 parts ECS resin to 12.5 parts ECS hardener (supplied by Uroxy Ltd). Afterwards, the mixture is mechanically stirred, ultrasonically agitated and degassed again. The entire procedure should be completed within 5 min. The resin mixture was filled into the glass fibre laminates (0/90, woven glass fibre GSM 194 (compression) or 500 (tensile), 4 layers) under vacuum (Fig. 1) with post curing for 12 h. The viscosity of epoxy resin with and without capsules was measured using Brookfield DV-II + Viscometer.

For the compression test, Wyoming Compression Fixture was used, following ASTM D6641 standard. The specimen size is 12 mm W × 140 mm L (transverse to fibre direction). All the tests were conducted in an Instron 1186 mechanical testing machine.

Fig. 2. The tensile test set up.