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Toughening and healing of continuous fibre reinforced composites by supramolecular polymers

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Interleaves comprising self-healing materials based on hydrogen bonded supramolecular polymers (SP) were successfully incorporated in the mid-plane of unidirectional (UD) carbon fibre reinforced polymers (CFRPs). The fracture toughness of these hybrid composites and their healing capability were measured under mode I loading. The fracture toughness appeared to have increased considerably since the maximum load (P_{max}) of the hybrid composite had increased approximately 5 times, and the fracture energy I (G_{IC}) displayed a dramatic increase by almost one order of magnitude when compared to the reference composite without the SP. Furthermore, the double cantilever beam (DCB) hybrid composites displayed a healing efficiency (H.E.) value for the mode I interlaminar characteristics around 60% for the P_{max} and the G_{IC} after the first healing cycle, dropping to 20–30% after the seventh cycle. During the mode I interlaminar fracture toughness tests the acoustic emission (AE) activity of the samples was also monitored. It was found that AE-activity strongly reduced due to the presence of the SP. Moreover, optical microscopy not only showed that the epoxy matrix at the interface is partly infiltrated by the SP, but it also revealed that cross-sections of both fractured surfaces were covered with the SP comprising pulled-out carbon fibres, indicating a strong interfacial adhesion. Finally it was shown that the SP fractured surfaces were partially covered with pulled-out carbon fibres emanating from the edges of the SP film in which the epoxy system exists.

1. Introduction

During the last decades the use of carbon fiber reinforced polymers (CFRPs) has been rapidly increased. Their enhanced specific properties make them attractive for structural applications in emerging fields of industrial technology such as aerospace, automotive, rail, marine, as well as the defense industry. One of the most important mechanical characteristic of fiber-polymer composites is their resistance to delamination. The interlaminar fracture toughness plays an important role in damage formation and propagation in FRPs. The presence of delaminations may lead to a loss of stiffness which can be a very important design consideration and may result to complete failure of the composite structure. It is therefore obvious that the delamination resistance of a laminate is critical for the in-service performance of structural composites and reliable non-destructive evaluation techniques are required for its early detection. In addition, high performance composites are sensitive to microcracking formation within the material due to in-service induced mechanical and thermal loading. Joining of microcracks under service loads may be another way for delamination. In general, both extensive microcracking and/or delaminations lead to rapid degradation of the materials performance. The composites conventional repair techniques are expensive, time consuming, and practically not applicable in the case of invisible defects. Thus, the widespread utilization of composites especially in human safety critical applications is always accompanied with damage diagnostic tools. This challenging situation acted as an inspiration for the seeking of new repair methods; cheaper, faster, and easier, applied at the early stages of damage formation. Self-healing materials [1,2] have been proposed as an emerging method of improving the performance of materials. This technology has been recently applied to composites and promises to extend the effective life-span of them, to reduce the maintenance

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needs and costs, and to improve the damage tolerance and reliability of composite structures.

A constant concern of various researchers has been the enhancement of the fracture behavior of high performance structural composites. A variety of methods are proposed in the literature which includes interleaving, hybridization, stitching, short-fibres, and z-pinning [3–7]. Kostopoulos et al. [8] achieved the 100% increase in the fracture energy after the addition of 1% CNF in the matrix of CFRP laminates. Magniez et al. [9] succeed the toughening of the CFRPs by interleaving a thin layer (~20 μm) of electrospun poly(hydroxyether of bisphenol A). This type of enhancement improved the fracture toughness in mode I and mode II by up to 150% and 30% respectively. Masahiro's et al. [10] experimental results about hybrid laminates, showed an increase at the rate of 50% for the fracture toughness, in mode I fracture test compare to the base CFRP laminates. Furthermore, the results of the mode II fracture toughness test confirmed that the interlaminar fracture toughness for hybrid laminates is 2–3 times greater than the base CFRP laminates. Kostopoulos et al. [11] dealt with the use of CNFs and PZT particles as dopants for the epoxy matrix of CFRP laminates. The presence of CNFs led to a remarkable increase in the mode I fracture energy of the laminates (about 100%) whereas the addition of PZT particles demonstrated reduction in the mode I fracture energy (G_{IC}). In mode II loading, both the CNFs and the PZTs improved the fracture properties of the CFRPs. Recently, Kostagiannakopoulou et al. [12] demonstrated the increase of the interlaminar fracture toughness of carbon fibre composites by modifying the epoxy matrix with graphene nano-species. Yasaee et al. [13,14] investigated the mode I and mode II fracture behavior of glass fibre reinforced plastics (GFRPs) with embedded strips of a thermoplastic strip, thermoplastic particles, chopped fibres, etc. From the various interleaved materials tested, those that improved the G_{IC} relatively to the baseline value were the polyimide thermoplastic film (79% increase), the chopped aramid fibres (46% increase), the 90° E-glass/epoxy prepreg strip (46% increase), the thermoset adhesive film (43% increase) and the chopped glass fibres (16% increase). All these interleaved strips had the potential to increase the G_{IIC} [14] with values from 75% to 123%.

Self-healing composites have previously been developed by embedding healing agents (i.e. reactive chemicals and catalysts) into the matrix using microcapsules that will release the healing agent upon crack damage [15,16]. Additionally, matrices with embedded vascular network have been developed in which the network serves as reservoir for the distribution of the healing system [17]. A different approach towards self-healing composites, are matrices that comprise thermoplastic polymers. Zako and Takano [18] were the first to achieve a restoration of the fatigue performance of FRPs comprising a thermoplastic-modified matrix. In a comparable approach, Hayes et al. [19,20] blended a polybisphenol A-based thermoplastic into the epoxy matrix in order to get up to 70% healing in the resulting FRP. Whereas, Pingkarawat et al. [21] were able to get a high recovery after healing in the quasi-static mode I fracture toughness in CFRPs with poly(ethylene-co-methacrylic acid) (EMAA) as thermoplastic modifier. Recently, Selver et al. [22] explored the healing potential of GFRPs of a matrix modified with glass-polypropylene hybrid yarns. The resulting composites displayed a 65% recovery from low-energy impact after a simple heating treatment. Interestingly, a synergistic combination on improved toughness and self-healing in high performance composites, has been shown by Wang et al. [23] who incorporated rectangular-shaped patches of two copolymers (EMA and EMAA) into the mid-thickness of CFRPs.

A more promising approach for self-healing composites might be found by merging reversible bonds into epoxide networks, since this approach allows the healing to be unlimited as no chemicals are consumed. Indeed, when thermo-reversible cross-links based on Diels–Alder chemistry were in an epoxy network based on diglycidyl ether of bisphenol A (DGEBA), self-healing was observed after considered time (hours) of exposing the material to elevated temperatures [24]. In a more recent paper, GFRPs comprising Diels–Alder based thermo-reversible cross-links, showed good self-healing behavior combined with good compatibility with the glass fibers [25].

A new technology that could be beneficial for self-healing in composites has been built on supramolecular polymers (SP) [26,27]. Especially those based on reversible hydrogen bonding arrays show great promise for self-healing materials [28–31], since these materials can typically withstand multiple healing cycles without substantial loss of performance, as a consequence of the highly directional and fully reversible non-covalent interactions present within the polymer matrix. In this study, we have employed the ureiodypyrimidone hydrogen bonding unit (UPy) as developed by Meijer and coworkers [32] because of its strong self-association, its synthetic accessibility, and the highly dynamic nature of low glass transition temperature (T_g)-polymers comprising the UPy [33]. Most interestingly, UPy-polymers have recently been shown to give unprecedented toughening in polybutadiene based interpenetrating networks [34].

The scope of the present work is the use of flexible SP comprising UPy-moieties as interleave additives into conventional unidirectional (UD) CFRPs in order to enhance the fracture properties of these hybrid composites and to take advantage of the SP's healing capability. This study is presenting an overview of the role of the SP in the fracture behavior and the repeatable ability to heal the cracks in CFRPs. The reference as well as the hybrid composites were subjected to mode I interlaminar fracture toughness tests and compared. After the fracture, the hybrid composites were subjected to heating under controlled loading in order to activate the SP interleave and the cracks to be healed. The healing process was repeated up to seven times. Finally acoustic emission (AE) recordings and optical microscopy examination led to better understanding of the involved failure mechanisms as well as some conclusions regarding the healing process.

2. Experimental

2.1. Materials

The composite materials which used in this study were fabricated by UD carbon fibre-epoxy prepreg CE-1007 150-38. The prepreg tape was supplied by SGL Group, Germany having a tensile strength of 2.4 GPa. The SP was the SPSH01 material as provided by Suprapolix that is based on a low T_g (−66 °C) polymer modified with UPy-moieties, and was chosen to play the role of the toughening and healing agent interleave in the present study. Fig. 1a depicts the originally received SPSH01 piece (approximately 45 mm × 30 mm × 5 mm), which has been further processed into films in the present work. This polymer owes its mechanical properties to the reversible, non-covalent interactions, such as hydrogen bonding, between the macromolecules.

2.2. Preparation of the SPSH01 interleaves and composite manufacturing

The preparation process of the SPSH01 interleaves is illustrated in Fig. 1. The as-received polymer piece (Fig. 1a) was converted into a thin film by a two-step heating/pressuring treatment (Fig. 1b) using a heat press machine. Firstly, the bulk SPSH01 block was pressured under 5 kN at 90 °C for 30 min. Then, thermal energy was stopped to be provided to the system and the SP material was left